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A STUDY ON THE SO-CALLED GARNIERITE FROM NEW CALEDONIA*

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ABSTRACT

Fourteen samples of the so-called garnierite from New Caledonia have been examined by means of X-ray diffraction, electron microscopy and diffraction, chemical and spectrochemical analyses, infrared absorption, differential thermal analysis and heat treatment. The presence of antigorite (platy serpentine), "talc", chrysotile (fibrous serpentine) and chlorite type minerals has been affirmed. The results of chemical analysis, infrared absorption and differential thermal analysis correlate to those structural types. Neither sepiolite nor nickel-bearing saponite, pimelite, has been found. Especially, the common occurrence of pimelite is rather doubtful. The results of attempt to synthesize nickel hydrosilicate are also presented.

Introduction

It has been well known that the green, nickel-bearing hydrosilicate generally called garnierite is not a specific mineral but a mixture of different hydrosilicates. The results of investigation in recent years[1) 3) 12) 15) 16)] on the so-called garnierite show a disagreement concerning the constituent mineral as summarized in Table 1, and some ambiguity still remains on the nature of garnierite.

Recently, Kinoshita and Tanaka[8) 9)] studied twenty samples of garnierite and deweylite and reported that these minerals were mixtures of two minerals analogous in structure to serpentine and talc, and the presence of a regular mixed layer of these two minerals which

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* Partly read at the Joint Meeting of the Mineralogical Society of Japan *et al.* held in Kyoto on Oct. 19, 1960.

Table 1. Constituent minerals of garnierite previously described.

Strunz (1957)[16]		Caillère (1936)[3]	Alekseeva (1936)[1]	Spangenberg (1938)[15]	Pecora (1949)[12]
(1:1)	Ni-antigorite (Nepouite) Ni-chrysotile (Garnierite)	Garnierite ○ Nourmeite	Garnierite Nepouite Connarite	Nepouite (Connarite) Garnierite	○ Garnierite
(2:1)	Ni-talc Ni-saponite (Pimelite) Ni-vermiculite	○	not exist	Pimelite	○
[(2:2)]	Ni-chlorite (?)			Schuchardite	
(chain)	Ni-sepiolite	○	not exist		

has 17Å. basal spacing. Kato and Minato[7] examined deweylite with X-ray diffraction and electron microscopy techniques and reached the conclusion that the mineral is a mixture of two minerals related to antigorite and talc, and that aquacreptite, iron or alumina rich variety, is presumably related to the non-swelling (2:1) layer silicate.

The purpose of this paper is to describe the constituent minerals of garnierite from New Caledonia. The results of chemical analysis, X-ray diffraction, electron microscopy and diffraction, infrared absorption, differential thermal analysis and the effect of heat treatment are given. Some results of attempt to synthesize nickel hydrosilicate are also presented.

Material and procedures of study

The materials used in this study are listed in Table 2. Most of them are selected from the ore samples from New Caledonia through the courtesy of Shimura Kako Company and Nippon Yakin Kogyo Company.

The approximate mean indices of refraction of the specimens determined by the immersion method range from 1.562 to 1.630, and generally the nickel-rich specimens have the higher indices.

X-ray diffraction was recorded with "Norelco" proportional counter unit. Filtered Cu$K\alpha$ radiation was used exclusively. Rate of

Table 2. General description of the garnierite specimens used in this study.

Specimen No.	Locality	Description	Nature of fragment	Mean index of refraction
1.	Poya	Green, massive, feels greasy.	Rounded thin plates.	1.562
2.	Poya	Light bluish green, crusty, soft.	Fine aggregates.	
3.	Poum	Light blue, massive, soft, with quartz.	Thin plates.	
4.	Poum	Light yellowish green, massive, with quartz, deweylite like.	Thin plates, zoning structure.	1.570
5.	Poum	Grass green, massive, compact.	Rounded thin plates.	1.573
6.	Pita	Pale grass green, massive, feels greasy.	Thin plates.	
7.	Pita	Dark green, crusty, feels greasy.	Thin plates.	
8.	Pita	Bluish green, crusty.	Fine aggregates.	1.564
9.	Theodie	Pale blue, botryoidal, with quartz.	Fine aggregates, zoning with quartz.	
10.	Thio	Bright bluish green, massive, feels greasy.	Thick plates.	1.573
11.	Thio	Pale greenish blue, massive, feels greasy, enclosing chromite.	Fine aggregates, zoning structure.	
12.	Thio	Dirty grass green, massive, compact.	Thin plates.	1.600
13.	Les Carrieres	Bright green, massive, with lustrous cleavage.	Fine aggregates.	1.630
14.	Nakety	Bright green, crusty, on limonitized dunite.	Fine aggregates.	1.585

scanning for recording ranged from 2° to ½° per minute, in 2θ. Effect of treatment with ethylene glycol was examined.

The specimens have been examined by electron microscopy and diffraction by using Hitachi instruments. The samples were crushed and lightly ground with a mortar and dispersed in water, and then

the fine fraction on collodion were examined before and after chromium shadowing.

Infrared spectra in the range from 2.5 to 16 microns were obtained by using either Nippon Bunko Model DS-201 or Hilger Model H-800 double beam recording infrared spectrophotometer, with a rock salt prism and with Nujol as the mounting medium.

The differential thermal analyses were made on several samples, which were heated at the rate of 10°C. per minute. The specimens were ignited at temperatures 500°, 750° and 1000°C. for the period of 1 hour, respectively, and the products formed on ignition were examined by X-ray diffraction, electron diffraction and infrared absorption.

Chemical analyses were made according to the standard methods. Besides, about a half of the specimens were spectrographically analysed.

Results and consideration

(1) *X-ray diffraction, electron diffraction and microscopy*

The mineral identification is based on characteristics of X-ray diffraction, electron microscopic appearance and diffraction and their response to glycolation and various heat treatments.

Their X-ray powder diagrams are illustrated in Fig. 1, and typical electron microscopic arpearance and electron diffraction patterns of the specimens are reproduced in Figs. 2～5 (Plates I and II).

From those results it has been concluded that at least four types of nickel-bearing hydrosilicate are present in the garnierite specimens. They are as follows;

(a) Nickel-bearing "antigorite" (platy serpentine): The 7Å. basal spacing disappers at about 450°C. Under the electron microscope it looks like a curled and rounded, thin plate or lath. Present dominantly.

(b) Nickel-bearing "talc": Identified by 10～11Å. spacing basal reflection which is not affected by glycolation or heat treatment at

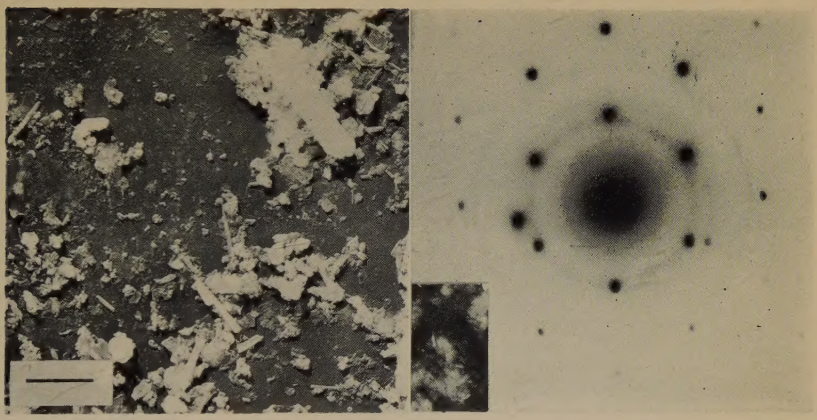

Fig. 2. Electron photomicrograph and diffraction pattern of nickel-bearing "antigorite" from Poum, New Caledonia (Specimen No. 5).

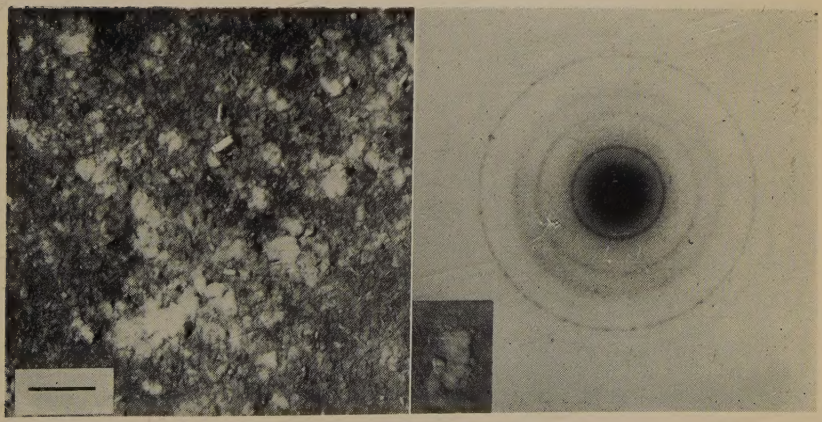

Fig. 3. Electron photomicrograph and diffraction pattern of nickel-bearing "talc" from Poya, New Caledonia (Specimen No. 6).

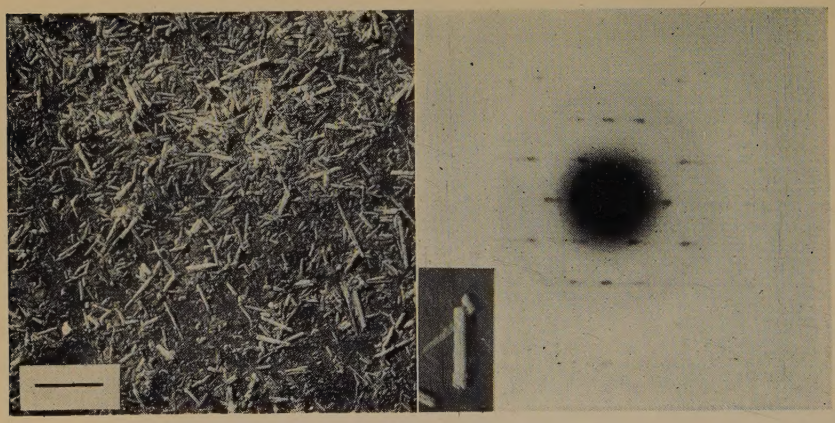

Fig. 4. Electron photomicrograph and diffraction pattern of nickel-bearing "chrysotile" from Poum, New Caledonia (Specimen No. 3).

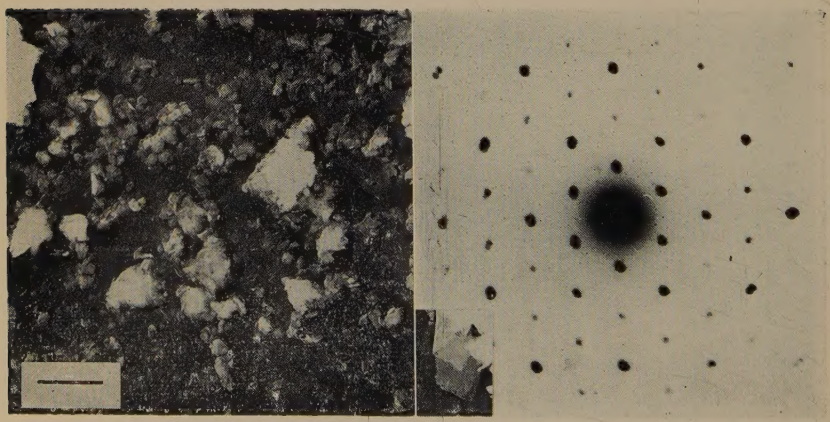

Fig. 5. Electron photomicrograph and diffraction pattern of nickel-bearing "chlorite" from Poya, New Caledonia (Specimen No. 1).

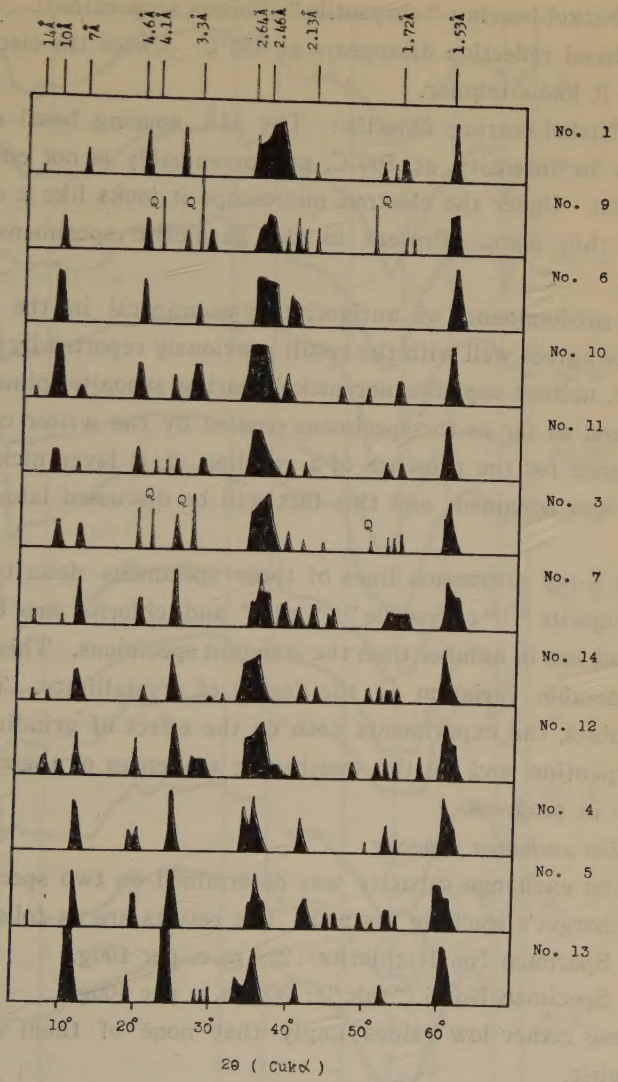

Fig. 1. X-ray powder diagrams for garnierites. (Q : quartz)

500°C. Under the electron microscope it looks like an irregular, very thin plate or aggregate. The garnierite specimens which are associated with botryoidal quartz generally consist of this mineral.

(c) Nickel-bearing "chrysotile" (fibrous serpentine): The 7Å. spacing basal reflection disappears at 450°C. Under the electron microscope it looks tabular.

(d) Nickel-bearing chlorite: The 14Å. spacing basal reflection increases in intensity at 500°C. and presumably is not effected by glycolation. Under the electron microscope it looks like a curled or rounded thin plate. Present in the garnierite specimens rich in alumina.

The predominance of antigorite type mineral in the so-called garnierite agrees well with the result previously reported by Caillère[3]. However, neither sepiolite nor nickel-bearing saponite, pimelite, has been found so far as the specimens studied by the writer concerned. No evidence for the presence of a swelling (2:1) layer nickel-hydrosilicate was obtained, and this fact will be discussed later in some detail.

The X-ray diffraction lines of those specimens described above as "antigorite", "chrysotile", "talc" and chlorite are broad and weak, and less in number than the standard specimens. This suggests a considerable variation in the degree of crystallinity. To clarify these points, the experiments both on the effect of grinding of talc and serpentine and on the weathering sequences of these minerals are now in progress.

(2) *Cation exchange capacity*

Cation exchange capacity was determined on two specimens by Schlloenberger's leaching method. The results are as follows;

Specimen No. 1 (chlorite): 26.8 m. e. per 100g.,

Specimen No. 6 ("talc"): 30.2 m. e. per 100g.

These rather low values imply that none of them are montmorillonitic.

(3) *Infrared absorption*

The spectra obtained are reproduced in Fig. 6. Each specimen shows strong absorption in the 9~11 microns region, which is characteristic of silicates in general. The details of the absorption curve

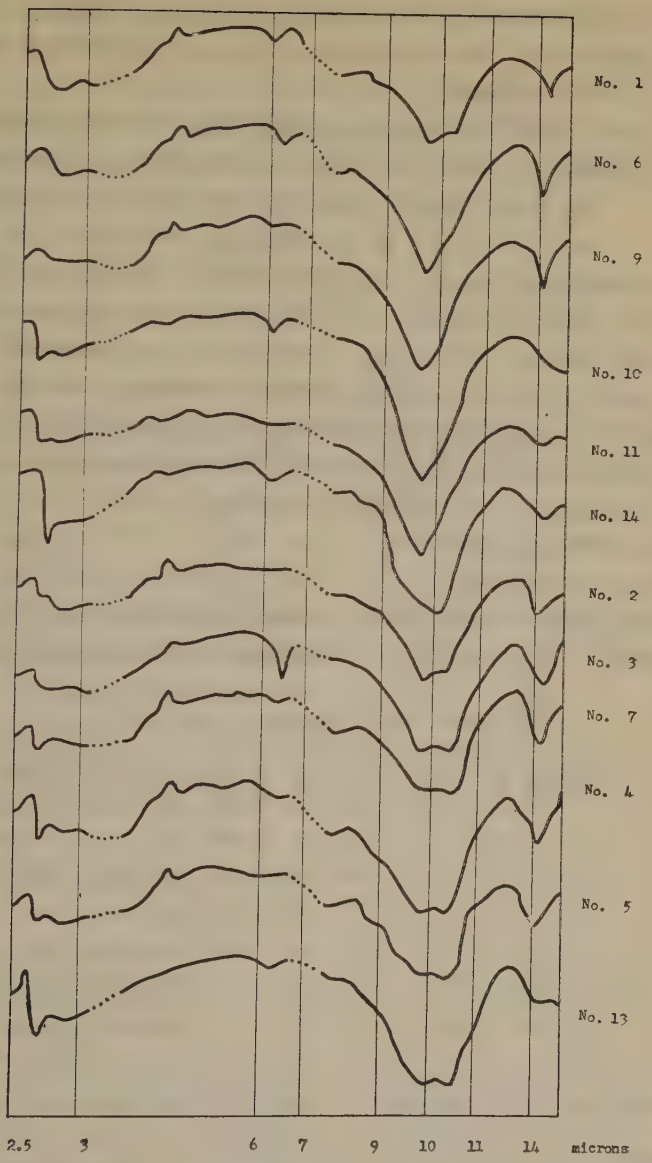

Fig. 6. Infrared spectra for garnierites.

in this region, however, differ among specimens as follows;

serpentine: two strong absorption peaks at about 9.8 and 10.4 microns,

talc[5]: only one strong absorption peak at about 9.8 microns,

chlorite[19]: absorption peaks at about 9.8 and 10.2 microns, the latter being of shoulder-type and variable with the alumina content of the mineral.

The absorption ranges from 2.5 to 7 microns are due to hydroxyl and to the water molecules. The intensities of absorption at about 6.2 microns due to the bending vibration of water molecule were rather weak and it seems rather curious. Although, the theoretical explanation for the absorption bands in the 2.6 to 3.0 microns region is not entirely clear, it is to be noted that the absorption at about 2.71 microns due to the stretching vibration of OH is more clear on the serpentine-type specimen.

(4) *Chemical composition*

Several specimens have been examined spectrochemically as shown in Table 3. The variation in the content of minor elements (Ag, Co,

Table 3. Minor elements in garnierite.

Locality	No.	Ag	Al	Ba	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	Si	Ti	V	Zn
Poya	1	0	⫲	0	⫲	0	+	+	±	⫲	⫲	±	+	⫲	+	0	0
	2	0	⫲	0	⫲	0	±	+	±	⫲	+	±	+	⫲	0	0	±
Poum	3	±	+	0	+	0	±	+	+	⫲	+	±	⫲	⫳	0	0	0
	4	±	0	0	+	0	+	⫲	+	⫳	⫲	⫲	⫲	⫲	0	0	0
	5	±	+	0	+	0	+	⫳	+	⫳	⫳	⫲	+	⫲	0	0	0
Pita	6	0	0	0	+	0	+	0	+	+	+	0	+	+	0	0	±
	7	0	±	0	⫲	0	+	+	+	⫲	⫲	+	⫲	⫲	0	0	±
Theodie	9	±	±	0	+	0	+	+	+	⫲	+	⫲	⫳	⫳	0	0	±
General intensity		W	w	0	w	0	w	w	W	S	S	w	S	S	w	0	W

⫳>⫳>⫲>+>±>0 general intensity S>s>w>W>0

Cr, Cu and Zn) may be correlated not to their structural types but to their localities.

Chemical analyses of the specimens are given in Table 4. The relation between the molecular ratios of RO and $H_2O(+)$ calculated on the basis of $SiO_2=4.00$ are shown in Fig. 7. Those recent analyses[2)4)10)17)18)] of garnierite and the related minerals in which $H_2O(+)$ and $H_2O(-)$ were separately analysed are also plotted for comparison.

The most outstanding feature in these analyses is the linear relation between RO and $H_2O(+)$ as obvious in Fig. 7. The ratios of $RO_2:RO$ for the analysed specimens range from (4:3) to (4:6), therefore they may be most simply interpreted as mixtures of serpentine and talc or saponite, as previously reported by Pecora *et al.*[12)]

The specimens generally contain $H_2O(+)$ in excess, a part of which will be attiributed to the presence of zeolitic water judging from the thermobalance curves.

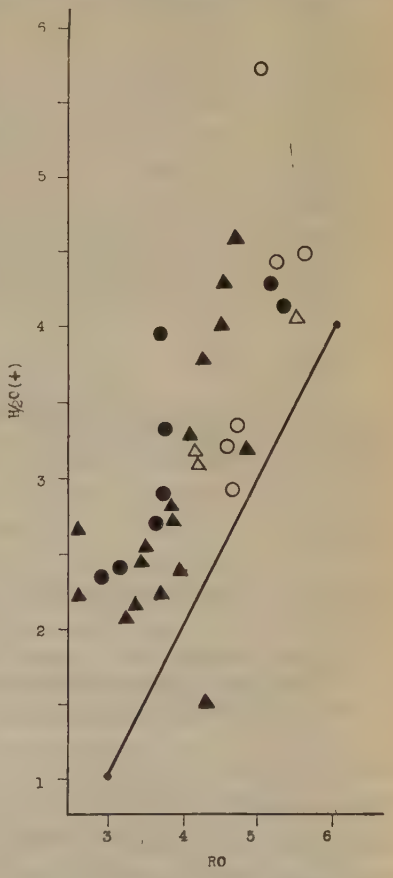

Fig. 7. Relation between RO and $H_2O(+)$ in garnierites and deweylites. ($SiO_2=4.00$)
Garnierite in this study ●
previous work ▲
Deweylite ○

(5) *Thermal study*

The differential thermal curves are reproduced in Fig. 8 together with those previously reported. They display the characteristics of two types of

Table 4. Chemical analyses and

Locality		Poya		Poum			
No.		1	2	3	4	5	6
Chemical composition	SiO_2	39.39%		50.00%	37.91%	37.40%	43.90%
	Al_2O_3	17.51		2.08	1.99	3.29	3.40
	Fe_2O_3	0.58		0.26	1.85	4.50	0.22
	NiO	4.21		7.80	6.39	6.05	15.68
	MgO	21.78		16.82	30.55	29.11	19.22
	K_2O	0.07		0.07	0.11	0.13	0.08
	Na_2O	0.03		tr.	0.03	0.25	tr.
	$H_2O(+)$	11.86		8.92	11.72	12.07	9.49
	$H_2O(-)$	4.76		11.21	10.09	7.60	8.81
	Total	100.19%		99.36%	100.64%	100.40%	100.79%
* RO					5.35	5.14	3.77
$H_2O(+)$					4.13	4.30	2.90
Under the electron microscope		rounded thin plates	rounded thin plates	tubes and fine plates	thin plates and some tubes	thin plates and some tubes	fine plates
Products on ignition**		E+F		E+F+(Q)	F	F+(E)	F
Identified minerals		chlorite	antigorite	chrysotile, talc, quartz	antigorite	antigorite	talc

Chemical analysis, by T. Kato (1960).

* Molecular ratio calculated on the basis of SiO_2=4.00.

** E: enstatite, F: forsterite, Q: quartz.

hydrosilicates, (2:1) layer and (1:1) layer. The former loses its absorbed water at about 150°C., its hydroxyl water at about 750°C., and passes into crystalline mixture of enstatite and/or forsterite with no marked exothermic peak. The latter is dehydrated at about 150°C., and at 800°C. it takes an amorphous form, which crystallizes at 815°C. with a marked evolution of heat to enstatite and forsterite. The curve for the chlorite type specimen, No. 1, is rather similar to the latter.

characteristics of the garnierite studied.

Pita		Theodie	Thio			Les Carrieres	Nakety
7	8	9	10	11	12	13	14
	39.70%	49.15%	44.28%	41.92%	35.75%	26.52%	39.15%
	2.14	1.82	2.93	8.48	3.09	1.21	2.68
	0.14	0.08	1.90	0.81	2.91	0.36	0.54
	30.88	18.60	31.14	22.10	36.20	49.45	34.92
	7.61	11.30	5.42	10.59	3.08	5.10	5.15
	0.11	0.08	0.05	0.02	0.02	0.04	0.03
	tr.	0.03	0.09	0.04	0.07	0.04	0.05
	7.93	4.69	7.82	7.61	9.02	10.80	11.45
	11.34	12.70	7.82	9.73	10.38	5.99	5.81
	99.85%	98.46%	100.36%	100.68%	100.52%	99.51%	99.78%
	3.68		2.97	3.19	3.76	7.82	3.69
	2.69		2.35	2.41	3.35	5.94	3.95
tubes and fine plates	thin and fine plates and tubes	fine plates	thin and fine plates	rounded thin plates	rounded thin and fine plates	rounded thin plates	thin plates, lath, some tubes
		F+(Q)	F	E+F	F	F	F
serpentine, talc	serpentine, talc	quartz, talc	talc, antigorite	talc, chlorite	talc, antigorite	antigorite	serpentine, talc

The products formed on ignition are affected by the Ni : Mg ratio of the specimens. Magnesium-rich specimen changes to forsterite and/or enstatite whereas nickel-rich one to forsterite only. This fact is in good agreement with previously reported results that forsterite occurs in both $MgO\text{-}SiO_2\text{-}H_2O$ and $NiO\text{-}SiO_2\text{-}H_2O$ systems while enstatite in the former system exclusively[13], and that in Mg-Ni pyroxene system nickel-bearing enstatite appears only in the nickel-poor region*.

* Hayashi, H. and S. Naka : a paper read at the Joint Meeting of the Mineralogical Society of Japan *et al.* held in Kyoto in November, 1960.

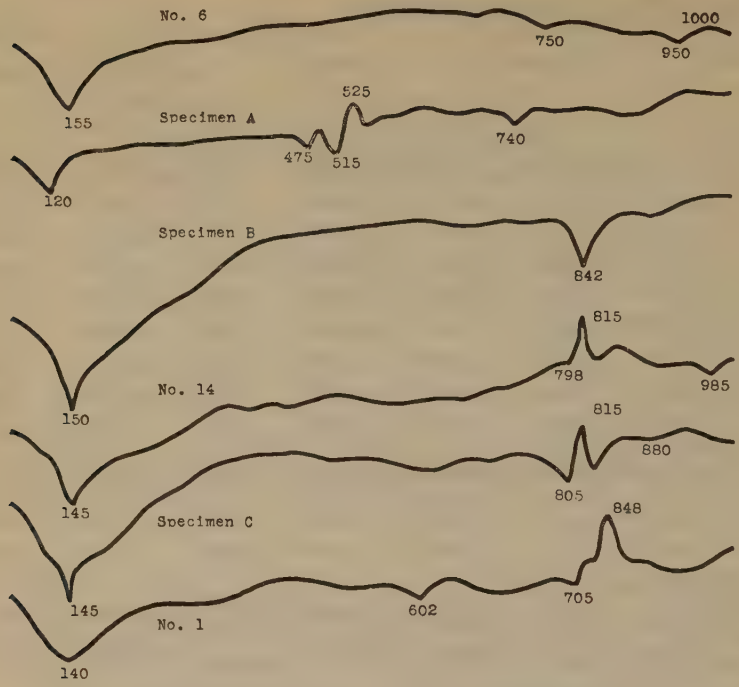

Fig. 8. Differential thermal curves for garnierites and deweylites. The curves for the specimens previously reported[8] are reproduced.

Specimen A: A mixture of "talc" type garnierite and quartz from New Caledonia.

Specimen B: "Talc" type deweylite (aquacreptite) from the Hirosé mine, Japan.

Specimen C: A mixture of "talc" type and "antigorite" type deweylite from the Kiuragi mine, Japan.

(6) *Synthesis*

Several papers have been published on the synthesis of nickel hydrosilicate. A nickel smectite, presumably trioctahedral, has been synthesized by van Voorthuijsen and Franzen[20]. The differential thermal curve would suggest that it is analogous to saponite.

Roy and Roy[13] have investigated the phase equilibrium relations in the system NiO-SiO_2-H_2O and have synthesized pure nickel garni-

erite in a wide range of temperatures and pressures. The tabular structure was formed only when alkalies were present. (This agrees with the results reported by Noll and Kircher[11]). To make the matter more clear, the mixtures of silica-gel and nickel-chloride hydrate were treated hydrothermally. The results are summarized in Table 5.

Table 5. Hydrothermal synthesis of nickel hydrosilicates.

Starting material composition	Temp. (℃.)	Press. (psi)	Times (hrs)	Product
$6NiO : 4SiO_2$	450	16, 000	24	Forsterite
$3NiO : 4SiO_2$	450	16, 000	24	Forsterite
$6NiO : 4SiO_2$	380	10, 000	48	Enstatite, Forsterite
$3NiO : 4SiO_2$–NaCl	380	10, 000	48	" Talc "
$3NiO : 4SiO_2$	380	10, 000	48	Enstatite
$6NiO : 4SiO_2$	350	8, 000	48	" Antigorite " (v. fine plates)
$3NiO : 4SiO_2$	350	8, 000	48	" Talc "
$3NiO : 4SiO_2$–NaCl	350	8, 000	48	(Talc)

The attempt to synthesize a swelling nickel hydrosilicate was failed.

Recently, Gillery[6] has examined the effect of the hydrothermal conditions on the production of the Mg-Al chlorite and the serpentine polytypes, and showed that the increase in the alumina contents favours the formation of platy serpentines. However, the results in Table 4 do not show any clear relation between the chemical composition and the morphology of the nickel-bearing serpentines. This will be due either to that the present analysis does not always follow the chemical conditions in which the minerals have been formed or to the presence of minor impurity.

Summary and discussion

The extremely wide variation in chemical composition of the nickel-bearing hydrosilicate has been recognized, and many different

varieties were discovered and named primarily on the basis of chemical analysis. These names include nickel-gymnite, genthite, noumeite, garnierite, nepouite, schuchardite, röttisite, connarite, revsdinskite, maufite, pimelite and deweylite.

However, later examination in the light of X-ray investigations has revealed that almost all of these minerals are not specific minerals but either closely related if not identical to garnierite or mixtures of different hydrosilicates.

In this report, the results of investigation on the so-called garnierite from New Caledonia have been described. The examined specimens consist essentially of serpentines ("antigorite" and "chrysotile"), "talc" and chlorite type minerals. The chemical composition, infrared absorption and differential thermal curves correlate to their structural types. It agrees well with Caillère's concept that "antigorite" is the essential component mineral of the so-called garnierite. Neither sepiolite nor nickel-bearing saponite, "pimelite", has been found in the garnierite specimens. In particular, the common occurrence of "pimelite" is rather doubtful, judging from the results obtained by the writer as well as by Kinoshita and Tanaka[8]. It is probable that non swelling (2:1) layer hydrosilicate analogous in structure to talc, has hither-to been mistaken for "pimelite"*.

Finally, the problem concerning the environments in which nickel-bearing hydrosilicates of these types have been formed is still left open. The intimate association of serpentine type and "talc" type garnierites suggests that there is little difference between their conditions of formation. On the other hand, the fact that almost all the garnierite accompanied by quartz of probably opal origin belongs to "talc" type seems to imply that the silica-rich environments may have favoured the formation of garnierite of this type.

---

* Some confusion has occurred in the nomenclature of "pimelite". Strunz[10], Spangenberg[15], Pecora *et al.*[12] consider this to be a variety of saponite but Winchell[21] to be a talc. Recently, Slansky[14] has showed that pimelite does not belong to the montmorillonite group, and this agrees with my concept.

Acknowledgements

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DATOLITE FROM THE OBIRA MINE, ÔITA PREFECTURE, JAPAN

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Abstract

Datolite of the Ginjiki deposit of the Obira mine is white to pale greenish white in colour and massive, occurring in association with skarn minerals. Refractive indices are: $\alpha=1.6273$, $\beta=1.652\sim1.655$, $\gamma=1.666$, and $(-)2V$ is $73°\pm1.5°$. The chemical composition is as follows; SiO_2 37.64, Al_2O_3 0.32, FeO 0.22, MnO none, CaO 34.90, MgO 0.60, B_2O_3 21.31, $H_2O(+)$ 5.66, total 100.65%. Trace of Ge is also contained. When weathered, it alters to a clayey mineral and decreases in the B_2O_3 content. It is paragenetic with quartz, calcite, stilpnomelane and grunerite (?), and includes or replaces skarn minerals of earlier stage. Hence, it must have been formed under hydrothermal condition in a relatively later stage of mineralization.

Introduction

The metallic ore deposits, inclusive of the Obira mine, in the areas around Mt. Sobo-san on the border of Ôita and Miyazaki Prefectures are well known for occurrences of boron minerals such as axinite, danburite, datolite and tourmaline. Previously, attention was paid to these deposits as boron resources. Occurrence of datolite has been known at the following three localities[2) 3) 7)] (Fig. 1);

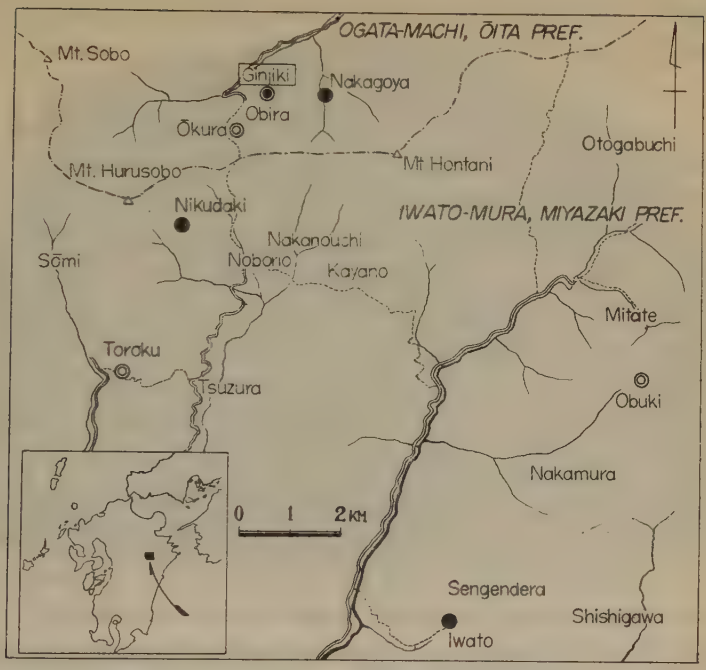

Fig. 1. Localities of danburite and datolite.
◎ Danburite, ◉ Danburite & datolite, ● Datolite.

Nakagoya, Obira Mine, Ôita Prefecture*,
Nikudaki, Noborio Mine, Miyazaki Prefecture**,
Iwato Copper Mine, Miyazaki Prefecture***.

At these localities, beautiful crystals of datolite have been collected from druses of skarn, but they are seldom found these days. In 1952, the writers discovered "massive datolite" abundantly distributed in the Ginjiki**** skarn zone, Obira Mine, showing the mode of occurrence different from any of the known cases. The writers first mistook the mineral for opaline quartz, because of its external appearance, but later it was confirmed to be datolite after physical, chemical and X-ray investigations. Part of the data was already

* 大分県尾平鉱山中小屋. ** 宮崎県登尾鉱山ニクダキ. *** 同県岩戸銅山. **** 銀鋪.

reported[5) 8)], and the present paper deals with the details of the mineral and genetical consideration.

Occurrence

The ore deposits of the Obira mine consist of Sn-Cu-As veins and Pb-Zn pyrometasomatic deposits. The Ginjiki deposit, belonging to the latter type, yields the datolite in question along with many minerals. The area where the deposit occurs is composed of the Palaeozoic (Silurian?) complex consisting of limestone, banded chert, slate and schalstein, accompanied by sheared biotite granite, all being zonally arranged with the general strike of northeast. The Miocene granitic rocks which are distributed on the west penetrating those rocks are regarded as ore bringers. The pyrometasomatic deposits occur in a limestone bed which was replaced by hedenbergite-garnet- skarn. Ore minerals are sphalerite and galena, accompanied by such gangue minerals as silicates and boro-silicates. Among them, the ortho-skarn formed in earlier stage, i. e. pyroxene-garnet skarn, shows a banded arrangement concordant with the structure of the limestone bed, and lead and zinc minerals are disseminated chiefly in aggregates of hedenbergite crystals. Network veins of axinite penterate or replace these ortho-skarn minerals. Danburite is found locally, and is usually rare.

Datolite, in association with other hydrothermal minerals such as stilpnomelane, grunerite, quartz and calcite, includes or replaces the skarn minerals of earlier stage. Especially it includes idiomorphic crystals of axinite and lievrite (Figs. 2~4, Plate I), and characteristically forms fairly large masses of white colour. On the other hand, it occurs in irregular association with massive quartz; in such a case, they are often mistaken for one and the same mineral as both minerals are pale greenish white in colour. Extremely fine-grained fibrous amphibole (grunerite?) and spherulitic stilpnomelane are included in datolite. Due to weathering, datolite sometimes alters to a clayey mineral.

Fig. 2. Macrophotograph showing massive aggregate of datolite (*d*) associated with axinite (a) and lievrite (1). (×2.7)

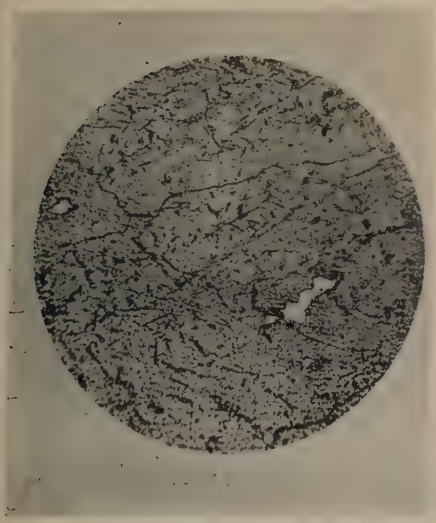

Fig. 3.

Fig. 4.

Figs. 3, 4. Photomicrograph of the thin section of datolite. Fig. 3. Polarizer only. Fig. 4. Crossed nicols. (×30)

Physical and optical properties

Datolite in the Ginjiki deposit has a glassy lustre and the colour ranging from milky white to greyish white or pale greenish white, but in thin section it is colourless. It is translucent when fresh, but in many cases it is almost opaque. Megascopically, datolite is compact and massive, displaying no crystal forms, but under the microscope it is revealed to be an aggregate of crystals. Table 1 shows the optical properties of datolites from Ginjiki and some other localities.

Table 1. Optical properties of datolites.

		1	2*	3	4	5*
Refractive indices	α	1.6273	1.6259	1.626	1.627	1.6261
	β	1.652～1.655	1.6535	1.654	1.654	1.6537
	γ	1.666	1.6699	1.670	1.668	1.6701
(−) $2V$		73°±1.5°	74°8′	74°±1°	73°	74°7′

* D-line, room temperature.

1. Ginjiki, Obira mine, Ôita Prefecture.
2. Noborio, Miyazaki Prefecture (by Harada[1]).
3. Iwato copper mine, Miyazaki Prefecture (by Harada[2]).
4. Hoino, Tanbara, Ehimé Prefecture (by Kato, Kanehira and Horikoshi[4]).
5. Hol Kol mine, Korea (by Harada[1]).

Chemical properties

The result of chemical analysis of the datolite is shown in Table 2. The formula $H_{1.00}Ca_{1.03}B_{0.98}Si_{1.00}O_{5.00}$, obtained through the analysis, closely agrees with that of the ideal datolite, viz., $HCaBSiO_5$ or $Ca(SiO_4)(OH)$. Flame-colouration is bright green due to the presence of boron.

The Ginjiki datolite often alters due to weathering into a white clayey mineral whose chemical composition, as mentioned below, reveals a decrease in B_2O_3 and an increase in H_2O as compared with

Table 2. Chemical composition of datolite from Ginjiki, Obira mine.

	Wt. %	Mol. prop.	Atomic ratio			
SiO_2	37.64%	627	Si	627		0.99_9
Al_2O_3	0.32	3	Al	6		
FeO	0.22	3	Fe	3	647	1.03_1
MnO	—	—	Mg	15		
CaO	34.90	623	Ca	623		
MgO	0.60	15	B	616		0.98_2
B_2O_3	21.31	306	H	630		1.00_4
$H_2O(-)$	—	—	O	3137		5.00_0
$H_2O(+)$	5.66	315	Formula	$H_{1.00}Ca_{1.03}B_{0.98}Si_{1.00}O_{5.00}$		

Analyst: N. Tanaka.

the unaltered sample.

SiO_2 36.38, Al_2O_3 0.50, Fe_2O_3+FeO 0.80, CaO 34.20, MgO 1.28, B_2O_3 19.18, $H_2O(-)$ 0.10, $H_2O(+)$ 6.82, total 99.26%

(Analyst, N. Tanaka).

Besides these major constituents, the Ginjiki datolite contains 0.01 to 0.05% Ge, as is known from the result of spectroscopic analysis. The germanium-bearing minerals in the Ginjiki deposit are datolite, lievrite and sphalerite[6].

X-ray determination

The X-ray data of datolite from Obira and other localities are given in Table 3. The respective specimens show a close similarity to each other.

Genesis of the Ginjiki datolite

The sequence of mineralization of the Ginjiki deposit is remarkably complex, as Table 4 indicates. As to the formation of skarn, two stages can be considered, i.e., the formation of garnet-pyroxene and that of boron-silicates. In the latter stage, that is, by boron-metasomatism, a large quantity of axinite and a small quantity of danburite crystallized out. Datolite, however, was not formed in such

Table 3. X-ray data for datolites.

Obira*		Hoino**		Hol Kol**	
d(Å)	I	d(Å)	I	d(Å)	I
5.99	10	6.02	5	6.02	5
4.83	20	4.84	10	4.84	10
3.766	60	3.77	40	3.77	30
3.417	40	3.41	30	3.41	10
3.118	100	3.12	100	3.12	60
3.000	50	3.00	50	3.00	100
2.860	80	2.86	50	2.86	20
2.526	40	2.52	30	2.53	20
2.412	10			2.41	5
2.301	10	2.29	10	2.30	10
2.246	50	2.24	50	2.25	20
2.194	40	2.19	60	2.19	20
2.159	20	2.16	10	2.16	10
2.120	5				
2.078	10	2.08	10	2.08	5
2.038	10			2.04	5
1.997	30	2.00	20	2.00	10
1.907	10				
1.875	40	1.875	20	1.875	10
1.772	10				
1.747	5	1.748	5	1.748	5
1.722	20	1.719	5	1.723	10
1.662	20			1.663	5
1.647	30			1.646	10
1.621	5				
1.559	5				

* Norelco X-ray Spectrometer, Cu-$K\alpha$, 30 KV., 15 mA., 8-1-4.
** After Kato, Kanehira and Horikoshi[4].

pneumatolytic stage but is a product of the later hydrothermal mineralization. In other words, as far as the Ginjiki deposit is concerned, the skarnization was succeeded by the retrogressive alteration-mineralization, and many kinds of hydrothermal minerals as shown in Table 4 have been formed. The origin of boron in datolite is an

Table 4. The sequence of mineralization in the Ginjiki deposit.

earlier

I	a.	Andradite, wollastonite, hedenbergite.
	b.	Lievrite, sphalerite, galena.
	c.	Grunerite, tremolite, quartz, calcite.
II	a.	Axinite, danburite, epidote, quartz, vesuvianite, fluorite.
	b.	Datolite, stilpnomelane, ferrohastingsite.
III	a.	Arsenopyrite.
	b.	Fe, Zn, Pb, Cu, Bi, Sn-sulphides.
	c.	Boulangerite.

later

important problem, as it involves the question whether boron was derived from the magma due to ascending solution, or some boron-bearing mineral (danburite, for instance) which had crystallized in the earlier stage and was later decomposed and re-generated. The Toroku mine west of the Obira mine is noted for the abundant yield of danburite. According to M. Noda[9], negative crystals of danburite, are found in this mine. Hence, it is possible that danburite is decomposed by a certain kind of solution. This is an interesting problem for discussion of boron-metasomatism.

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MANGANPYROSMALITE FROM THE KYURAZAWA MINE, TOCHIGI PREFECTURE

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Abstract

Manganpyrosmalite $(Mn, Fe)_8Si_6O_{15}(OH, Cl)_{10}$ occurs abundantly as ore forming mineral at the Shinsanjin ore body of the Kyurazawa mine, Tochigi Prefecture, Japan. The first occurrence of pyrosmalite in Japan has been reported from another ore body of the same mine. The chemical analysis of the newly found manganpyrosmalite by J. Ito gave SiO_2 35.43, FeO 9.57, MnO 42.01, MgO 1.14, Al_2O_3 0.50, Cl 5.00, SO_3 0.17, $H_2O(\pm)$ 7.50, $-O=Cl_2$ −1.13, total 100.19%. Sp. gr. 3.12, hardness $4\frac{1}{2}$; $\varepsilon=1.631$, $\omega=1.667$, $\omega-\varepsilon=0.036$, uniaxial negative; lattice constants measured from the X-ray powder pattern are $a_0=13.42$Å, and $c_0=7.159$Å. The associated minerals are rhodonite, manganese amphibole, garnet, mangancalcite, quartz and small amounts of sulphide minerals. The chemical analysis of previously reported pyrosmalite from the Odaki ore body in this mine by H. Haramura came out as follows; SiO_2 33.50, TiO_2 0.08, Al_2O_3 0.11, Fe_2O_3 1.07, FeO 24.09, MnO 27.62, MgO 1.65, ZnO 0.04, CaO <0.02, $H_2O(-)$ 0.22, $H_2O(+)$ 6.53, P_2O_5 <0.02, Cl 5.63, $-O=Cl_2$ −1.27, total 99.31%. The correlation between the refractive indices and FeO contents of the minerals of friedelite-manganpyrosmalite-pyrosmalite series is given.

Introduction

Manganpyrosmalite, a manganese rich species of pyrosmalite has been first described from Sterling Hill, New Jersey, U. S. A. by Frondel and Bauer[3] in 1953 and the succeeding occurrence at Broken Hill, New South Wales, was found by Hutton[4] in 1956.

In June of 1958, the writers, on their second trip to the Kyurazawa mine*, from where the first occurrence of pyrosmalite in Japan was reported[6], discovered manganpyrosmalite mass from a newly excavated area of another deposit called Shinsanjin ore body. It is situated about four hundred metres northeast of the Odaki ore body where pyrosmalite and knebelite occur abundantly as essential ore-forming minerals and has been mined since 1956[6].

The writers will describe in this paper the mode of occurrence and the results of the chemical analysis and X-ray investigations of the manganpyrosmalite. The tentative correlation diagram between refractive indices and chemical compositions of the friedelite-manganpyrosmalite-pyrosmalite series will be presented as well.

Occurrence

It has been assumed that the Shinsanjin ore body possibly lies in the same stratigraphic horizon as the Odaki ore body, according to the northeast strike of the Palaeozoic formation of the surrounding area. The lens-shaped ore body was found in slightly metamorphosed massive and banded cherts. Its actual dimensions are around several metres both vertically and laterally with maximum width of two metres.

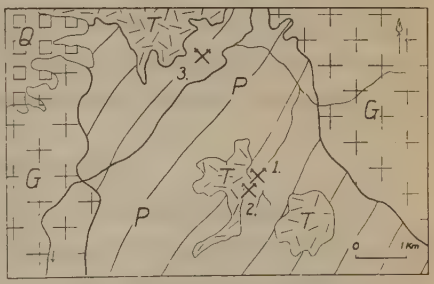

Fig. 1. Geological Map of the adjacent area of the Kyurazawa mine.
1. Shinsanjin ore body of the Kyurazawa mine.
2. Odaki ore body of the Kyurazawa mine.
3. Ashio Mine.
P: Palaeozoic formations.
G: Granodiorite.
T: Tertiary volcanics.
Q: Quaternary volcanics.

The manganpyrosmalite, one of the principal ore minerals in this ore body, is as-

* 栃木県上都賀郡足尾町久良沢鉱山.

sociated with rhodonite, manganese amphibole, garnet, quartz and some sulphides such as pyrrhotite, sphalerite and chalcopyrite. It occurs as a granular aggregate in various sizes from one centimetre to less than half a millimetre. A small amount of mangancalcite is also found as an interstitial material of manganpyrosmalite.

Under the microscope it displays a replacement texture. The associated anhydrous manganese silicates have been replaced by it as in the case of pyrosmalite-bearing ores from the Odaki ore body. Also, in the marginal part of ore body, manganpyrosmalite occurs replacing chert along the bedding planes or sometimes cutting through the chert as veinlet.

Crystal habit

From many drusy parts composed of coarse crystals, tabular crystals of manganpyrosmalite up to five millimetres in diameter were found associated with quartz crystals. Those are of very simple form and composed of only two forms, {0001} and $\{10\bar{1}0\}$. Zonal structure, which is commonly observed in the pyrosmalite from the Odaki ore body, was not found in this manganpyrosmalite.

Physical properties

The manganpyrosmalite is translucent and of pinkish colour a little lighter than that of associated rhodonite. After the prolonged exposure in sunlight the colour is easily faded. Basal cleavage is perfect and gives slight silky lustre on {0001}. Specific gravity 3.12 was measured by pycnometer method. Hardness is $4\frac{1}{2}$. The following optical properties were also obtained:

$\varepsilon=1.631$, $\omega=1.667$, $\omega-\varepsilon=0.036$,
Uniaxial and optically negative.

X-ray studies

The X-ray powder pattern of manganpyrosmalite was obtained by a Philips Geiger Counter X-ray diffractometer. The pattern was

compared with that of Sterling Hill material[3] and indexed in terms of hexagonal cell as in Table 1. The lattice dimensions of the manganpyrosmalite from Shinsanjin were calculated from the d values of $(44\bar{8}0)$ for a_0 and of (0005) for c_0 as follows:

$$a_0=13.42\text{Å}., \qquad c_0=7.159\text{Å}.$$

Table 1. X-ray powder patterns of manganpyrosmalite and pyrosmalite.

1.		2.		3.*				
d(Å)	I	d(Å)	I	d(Å)	I	Q_{obs}	Q_{cal}	$hkil$
11.6	30	11.65	1	11.68	1	0.0073	0.0074	$10\bar{1}0$
7.16	100	7.146	100	7.201	100	0.0193	0.0195	0001
6.71	10			6.722	½	0.0221	0.0222	$11\bar{2}0$
6.09	30	6.097	2	6.104	2	0.0268	0.0269	$10\bar{1}1$
5.77	10							$20\bar{2}0$
4.886	20			4.870	½	0.0421	0.0417	$11\bar{2}1$
4.509	10	4.501	1	4.505	½	0.0492	0.0491	$20\bar{2}1$
4.376	10	4.376	½	4.394	1	0.0517	0.0518	$21\bar{3}0$
3.736	20	3.740	½	3.742	1	0.0713	0.0713	$21\bar{3}1$
3.583	80	3.570	50	3.583	30	0.0778	0.0780	0002
3.419	40	3.411	3	3.427	7	0.0852	0.0854	$10\bar{1}2$
				3.420	7	0.0855	0.0861	$30\bar{3}1$
3.338	30							$22\bar{4}0$
3.035	20			3.050	1	0.1075	0.1076	$20\bar{2}2$
				3.043	1	0.1080	0.1083	$22\bar{4}1$
2.882	20			2.905	2	0.1185	0.1184	$40\bar{4}0$
2.770	20			2.784	1b	0.1295	0.1298	$21\bar{5}2$
2.683	90	2.686	10	2.692	20	0.1380	0.1379	$40\bar{4}1$
		2.622	½					$30\bar{3}2$
2.549	20							$41\bar{5}0$
				2.497	½	0.1604	0.1601	$32\bar{5}1$
2.385	20	2.382	1	2.388	2b	0.1753	0.1741	$31\bar{4}2$
							0.1749	$41\bar{5}1$
							0.1753	0003
2.334	10							$10\bar{1}3$
2.251	70	2.250	5	2.258	25	0.1962	0.1964	$40\bar{4}2$
							0.1981	$11\bar{2}3$

Table 1. (cont.)

2.102	10d			2.095	½	0.2278	0.2268	42$\bar{6}$1
							0.2274	21$\bar{3}$3
							0.2295	51$\bar{6}$0
1.843	40	1.839	2	1.846	10	0.2935	0.2934	43$\bar{7}$1
							0.2940	40$\bar{4}$3
1.768	10			1.765	½b	0.3209	0.3196	10$\bar{1}$4
1.733	10d							11$\bar{2}$4
1.672	50	1.675	1	1.678	5	0.3553	0.3553	44$\bar{8}$0
1.627	40	1.630	1	1.633	3b	0.3752	0.3748	44$\bar{8}$1
							0.3755	33$\bar{6}$3
				1.573	½b	0.4042	0.4044	62$\bar{8}$1
							0.4051	51$\bar{6}$3
1.523	50	1.5195	2	1.525	5	0.4298	0.4306	40$\bar{4}$4
				1.465	½b	0.4661	0.4663	63$\bar{9}$0
1.432	10	1.4270	2	1.432	2	0.4878	0.4878	0005
1.419	20			1.425	1	0.4927	0.4932	80$\bar{8}$1
							0.4939	61$\bar{7}$3
				1.422	1	0.4945	0.4947	10$\bar{1}$5
1.371	20							42$\bar{6}$4
								20$\bar{2}$5
1.342	20			1.344	½	0.5534	0.5539	30$\bar{3}$5
a_0	13.86Å.	13.40Å.		13.42Å.				
c_0	7.16Å.	7.135Å.		7.159Å.				
Sp. gr.	3.13	3.14		3.12				

1. Manganpyrosmalite from Sterling Hill, New Jersey, U. S. A.[3].
2. Pyrosmalite from the Odaki ore body, Kyurazawa mine, Tochigi Prefecture[6].
3. Manganpyrosmalite from the Shinsanjin ore body, Kyurazawa mine, Tochigi Prefecture.

* Cu/Ni radiation, slit : 1°—0.006″—1°, Scanning speed : 1°/2 min., scale factor : 8, multiplier : 1, time constant : 8 sec. The abnormally strong reflections from the basal spacings are undoubtedly due to preferred orientation. b : broad. d : diffuse.

Chemical compositions

The material used for chemical analyses was hand-picked from the coarse grained aggregates. An attempt to separate the disco-

loured mantle of the crystal chemically, was not successful because manganpyrosmalite is also readily soluble in dilute HCl. Therefore only very fresh and purest crystals were selected. The results of an analysis carried out by the third author while he was at Department of Mineralogy, Harvard University is given in Table 2.

Table 2. The chemical analysis of manganpyrosmalite from the Shinsanjin ore body, Kyurazawa mine, Tochigi Prefecture.

	Wt. %	Mol. no.	No. of metals	No. of oxygen	No. of mol.* in unit cell		Ideal number
SiO_2	35.43%	0.5899	0.5899	1.1798	12.38	12.59	12
Al_2O_3	0.50	0.0049	0.0098	0.0147	0.21		
FeO	9.57	0.1322	0.1322	0.1322	2.77	15.78	16
MnO	42.01	0.5922	0.5922	0.5922	12.42		
MgO	1.14	0.0283	0.0283	0.0283	0.59		
$H_2O(\pm)$	7.50	0.4163	0.8326	0.4163	17.46	20.42	20
Cl	5.00	0.1410	0.1410		2.96		
SO_3	0.17						
	101.32%			2.3635			
$-O=Cl_2$	−1.13			−0.0705			
Total	100.19%			2.2930	48.11 (O) =17.46 (for OH) +30.65 (for Si)		30

(by J. Ito, 1959)

* Molecular weight is calculated as 2098.

Based on the molecular weight calculated from the measured lattice constants and specific gravity, the chemical formula of the manganpyrosmalite from Shinsanjin was expressed as $(Mn_{12\cdot42}Fe_{2\cdot77}Mg_{0\cdot59})_{15\cdot78}(Si_{12\cdot38}Al_{0\cdot21})_{12\cdot59}O_{30\cdot65}[(OH)_{17\cdot46}Cl_{2\cdot96}]_{20\cdot42}$. This is very close to the ideal formula $(Mn, Fe)_8Si_6O_{15}(OH, Cl)_{10}$ advocated by Frondel and Bauer[3].

Also chemical analysis of the pyrosmalite from the Odaki ore body that was reported in the previous paper[6], was carried out lately by H. Haramura. The sample was carefully separated by hand picking from zoned pyrosmalite with minute grains of knebelite. The

result is given in Table 3. It is calculated in the same manner as described above and the empirical formula for the pyrosmalite from Odaki is given as $(Mn_{8.17}Fe_{7.31}Mg_{0.86}Zn_{0.01})_{16.35}(Si_{11.70}Ti_{0.02}Al_{0.05})_{11.77}O_{30.62}[(OH)_{15.23}Cl_{3.35}]_{18.58}$. This is also close to the ideal formula.

Table 3. The chemical analysis of pyrosmalite from the Odaki ore body, Kyurazawa mine, Tochigi Prefecture.

	Wt. %	Mol. no.	No. of metals	No. of oxygen	No. of mol.++ in unit cell		Ideal number
SiO_2	33.50	0.5578	0.5578	1.1156	11.70		
TiO_2	0.08	0.0010	0.0010	0.0020	0.02	11.77	12
Al_2O_3	0.11	0.0011	0.0022	0.0033	0.05		
Fe_2O_3	1.07+	0.0134	0.0134	0.0134			
FeO	24.09	0.3353	0.3353	0.3353	7.31		
MnO	27.62	0.3893	0.3893	0.3893	8.17	16.35	16
MgO	1.65	0.0409	0.0409	0.0409	0.86		
ZnO	0.04	0.0004	0.0004	0.0004	0.01		
CaO	<0.02						
$H_2O(-)$	0.22						
$H_2O(+)$	6.53	0.3628	0.7256	0.3628	15.23		
P_2O_5	<0.02					18.58	20
Cl	5.63	0.1588	0.1588		3.35		
	100.58			2.2630			
$-O=Cl_2$	−1.27			−0.0794			
Total	99.31			2.1836	45.85 (O)		
					=15.23 (for OH)		
					+30.62 (for Si)		30

(by H. Haramura, 1959)

+ Calculated as FeO.

++ Molecular weight is calculated as 2098.

The variation diagram of indices of refraction, ε and ω, versus FeO content of the friedelite-manganpyrosmalite-pyrosmalite series is illustrated in Fig. 2 using data cited from the published works of several authors and those from the present work as well. The ε versus FeO points are distributed along a smooth curve as shown in Fig. 2, while three ω versus FeO points of manganpyrosmalite are plotted quite apart from a possible smooth curve. Chlorine con-

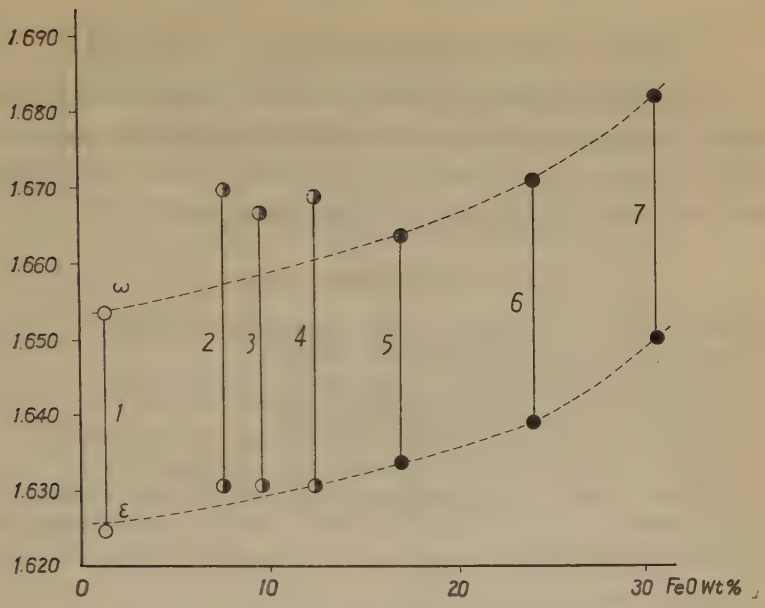

Fig. 2. Variations in the optical properties in the friedelite (open circle)-manganpyrosmalite (semi solid circle)-pyrosmalite (solid circle) series.

1. Friedelite from the Buckwheat mine, Franklin, New Jersey. After Bauer and Berman[1].
2. Manganpyrosmalite from Broken Hill, New South Wales. After Hutton[4].
3. Manganpyrosmalite from the Shinsanjin ore body, Kyurazawa mine, Tochigi Prefecture. This study.
4. Manganpyrosmalite from Sterling Hill, New Jersey. After Frondel and Bauer[3].
5. Pyrosmalite from the Broken Hill South mine, New South Wales. After Stillwell and McAndrew[5].
6. Pyrosmalite from the Odaki ore body, Kyurazawa mine, Tochigi Prefecture. After Watanabe and Kato[6] and this study.
7. Pyrosmalite from the Broken Hill North mine, New South Wales. After Stillwell and McAndrew[5].

tents of this series do not vary so significantly as to give a reasonable explanation of this problem, on which further study is necessary.

Acknowledgements

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KOBEITE FROM THE USHIO MINE, KYOTO PREFECTURE, JAPAN AND RE-EXAMINATION OF KOBEITE*

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ABSTRACT

A black prismatic kobeite-like mineral from a granite pegmatite of the Ushio mine in Ômiya town, Kyoto Prefecture and the kobeite from the original locality have been studied. Both the chemical analyses and the X-ray powder patterns of heated materials of the two minerals gave the concordant results. The two minerals contain notable amount of zirconium and after heat treatment give X-ray patterns similar to those of stabilized cubic zirconia.

Kobeite will not be a member of the euxenite-polycrase series but may be a distinct mineral species of multiple oxide containing Y, Fe, U, Ti, Zr and Nb as the main components.

Introduction

Kobeite was first described in 1950 by J. Takubo and others[1][2] at the Shiraishi pegmatite, Ômiya Town (Kôbé Village at that time), Naka County, Kyoto Prefecture** (Fig. 1). They regarded

* Read at the Joint Meeting of the Mineralogical Society of Japan *et al.* held in Kyoto on Oct. 19, 1960.

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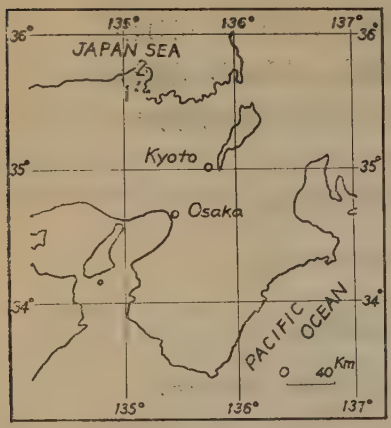

Fig. 1. Index map for locations of the Ushio mine (1) and the Shiraishi pegmatite (2), Kyoto Prefecture.

this mineral as an unusually niobium and tantalum poor member of the euxenite-polycrase series giving a name kobeite after the locality.

In 1957, Hutton[6] found a black slender prismatic mineral in a cobble of a graphic granite in gravels of the Paringa River, South Westland, New Zealand and identified as kobeite from the qualitative chemical tests and X-ray diffraction patterns.

In July of 1960, the first author collected a black prismatic radioactive mineral resembling kobeite from a granite pegmatite of the Ushio mine at Okuôno in Ômiya Town (Fig. 1)*, situated about 5 km. S.S.W. of the original locality. In order to identify the mineral, chemical analyses and X-ray studies were made on both the Ushio mineral and the kobeite from the original locality. In this paper the writers will present the results of them with considerations on the position of kobeite in mineral classification.

Occurrence

At the Ushio mine and in the vicinities, Late Cretaceous biotite granite forms the basement of Miocene volcanic rocks[5]. This granite involves many pegmatites such as at Ôro, Mié and Morimoto together with the Ushio mine and the Shiraishi pegmatite[11].

The very exposure where this mineral was collected is called the Second Ore Body of the Ushio mine. It is a composite dike composed

* 大宮町奥大野潮鉱山.

of an aplite with micrographic texture and a pegmatite with large crystals of quartz, microcline, oligoclase and a small amount of biotite in the core. The total width attains about four metres. It strikes N. 50° E. and dips 50° to NW, running nearly parallel to the Shiraishi pegmatite.

The mineral in question occurs as minute prism, about one millimetre in diameter, with striated faces and is embedded in oligoclase which is coloured deep red around it. Sometimes it forms a dendritic aggregate which is composed of chain of prisms and attains about five centimetres in length (Fig. 2). In rarer cases, it is thrust through a platy crystal of ilmenite.

The other minerals associated include allanite, radioactive zircon, magnetite, pyrite and fergusonite in the order of amount.

Fig 2. Radial aggregate of kobeite in oligoclase from Ushio mine.

Physical properties

This mineral is strongly radioactive and black with resinous lustre and has conchoidal fracture similar to many multiple oxides in metamict state. The streak colour is reddish brown. The hardness is about 5½ and the specific gravity measured by Berman balance is 4.60. In transmitted light, it is translucent and brownish yellow in colour and free from the inclusion of the other mineral. In places reddish brown parts are formed along minute fractures probably due to alteration. Both fresh and altered parts are entirely isotropic.

Table 1. The procedures applied to the analyses of kobeites.

Fuse about 0.2 g. of the pulverized sample with $NaHSO_4$, and treat the melt with 2% tannin solution in dilute H_2SO_4 (7% in weight). Warm the liquid on a water bath and set aside overnight.

Ppt. 1. Consisting chiefly of the tannin complexes of Nb and Ta. Ignite and weigh as $(Nb, Ta)_2O_5 + TiO_2 + SiO_2$. Determine SiO_2 by treating with HF and H_2SO_4, and TiO_2 by means of colorimetry.

Filt. 1. Evaporate, add HNO_3 to destroy the organic material, dilute, reduce the acid concentration with NH_4OH and saturate with H_2S. Test the sulphide ppt. for Pb and Sn. Boil to expel H_2S, add HNO_3 and neutralize with NH_4OH, filter and repeat the precipitation.

Ppt. 2. Contains rare earths, Th, Fe, Ti, Zr, U and Al. Dissolve in dilute HCl and evaporate to dryness. Add enough amount of 3% oxalic acid solution, stand overnight.

Filt. 2. Precipitate Mn by treating with $(NH_4)_2S_2O_8$.

Ppt. 3. Dissolve in dil. HNO_3 containing a few drops of H_2O_2, and titrate Mn by the usual arsenite method.

Filt. 3. Test for residual rare earths, and recover them if necessary. Then determine Ca and Mg by the EDTA chelatemetry.

Ppt. 4. Ignite and weigh as $(Ce, Y)_2O_3 + ThO_2$. Determine ThO_2 by the H_2O_2 method, and separate Ce group and Y group rare earths by saturating the solution with K_2SO_4.

Filt. 4. Add H_2SO_4, evaporate to fume to destroy oxalic acid, dilute, add tartaric acid and make alkaline by adding NH_4OH, then saturate with H_2S.

Ppt. 5. Consists of Fe_2S_3. Determine Fe_2O_3 by the oxidmetric titration.

Filt. 5. Adjust the concentration of H_2SO_4 to 10% by vol., cool the solution to 5~10°C., add enough amount of 6% cupferron solution.

Ppt. 6. Ignite and weigh as $TiO_2 + ZrO_2 + HfO_2$. Fuse with $NaHSO_4$, dissolve the melt in 4% H_2SO_4 by vol. Pass the solution through a Jones reductor, equipped with a receiver filled with $Fe_2(SO_4)_3$ solution. Titrate the solution of Fe^{2+} in the receiver with standard permanganate solution, and calculate the amount of TiO_2. Estimate $ZrO_2 + HfO_2$ by the difference, or by the ignition and weighing of their phosphates precipitated from H_2SO_4 solution.

Filt. 6. Evaporate and expel cupferron, make slightly basic with NH_4OH, add tannin.

Ppt. 7. Ash and then determine U and Al.

Filt. 7. Give up.

Chemical analyses

Samples selected by hand picking, panning and magnetic separation were subjected to the chemical analyses. The analytical procedures, specially designed by the second author for the present mineral, is shown in Table 1. The results of the analyses of the specimens from the Ushio mine, from Shiraishi and the original analysis of kobeite by Takubo and others[12] are listed in Columns 1,

Table 2. Chemical analyses of Kobeites.

	1	2	3
CaO	0.73%	0.53%	1.23%
MgO	0.79	0.50	1.28
MnO	1.48	2.16	0.84
Ce_2O_3			0.58
$[Ce_2O_3]$	1.64	1.83	1.63
$[Y_2O_3]$	21.98	24.40	22.21
U_3O_8	5.84	5.39	9.95
ThO_2	1.31	1.25	0.82
Al_2O_3	0.35	0.33	0.34
FeO			0.62
Fe_2O_3	9.55*	8.32*	12.93
$(Zr, Hf)O_2$	17.08	14.91	
TiO_2	26.02	26.21	34.72
$(Nb, Ta)_2O_5$	8.01	7.25	4.84
SiO_2	1.59	1.99	3.83
$H_2O(+)$	2.81**	3.87**	3.75
$H_2O(-)$	0.42	0.47	0.44
PbO	***	***	0.13
Total	99.60%	99.73%	100.14%

1. Kobeite. Ushio mine, Ômiya Town, Kyoto Prefecture. (Analyst: Kozo Nagashima, 1960).
2. Kobeite. Shiraishi pegmatite, Ômiya Town, Kyoto Prefecture. (Analyst: Kozo Nagashima, 1960).
3. Kobeite. Shiraishi pegmatite, Kôbé (Ômiya), Kyoto Prefecture. (Analyst: Jitsutaro Takubo, 1950)[12].

* Total iron. ** Ignition loss. *** Pb and Na were not determined.

2 and 3 respectively in Table 2. As seen from the results, it is quite remarkable that the two specimens analysed by the second author contain a marked quantity of zirconium, which was not determined in the original analysis, besides the normal constituents of the euxenite-polycrase series, and that there is no essential difference between the two samples taken from different localities. X-ray spectrochemical analyses were carried out for four crystals of kobeite from the original locality, and they all proved a high content of zirconium.

The average atomic weight of the yttrium group rare earths were calculated from the weight of the mixed oxide and the number of equivalence determined by the EDTA titration. They were found to be 118 for the Ushio specimen, and 121 for the Shiraishi specimen, showing that yttrium is predominant in rare earths in both specimens, and the results coincide with the data of X-ray spectrochemical analyses.

Regarding the loss on ignition as non essential, the results lead to the empirical formulae of $A_{1\cdot00}B_{2\cdot66}O_{6\cdot69}$ for the Ushio specimen and $A_{1\cdot00}B_{2\cdot37}O_{6\cdot15}$ for the Shiraishi specimen, where A=Y, Mn, U, Mg and Ca, and B=Ti, Zr, Fe^{3+}, Nb and Si.

X-ray studies

Both the mineral from Ushio and the kobeite from Shiraishi are in metamict state and no diffraction line was detected by X-ray spectrometer. So, they were heated in air at about 900°C. for one hour and re-examined. The X-ray powder patterns of heated materials are given in Table 3 (Columns 1 and 2). They closely agree with those of heated (at 620°C. for one hour in air) kobeites from the original locality and Paringa River presented by Hutton[6] except two faint lines with spacings 4.15Å. and 3.76Å. respectively (Columns 3 and 4). Hutton noticed that most of the diffraction lines can be indexed in terms of cubic uraninite-type cell and the cell constant of the Paringa River kobeite is 5.029Å. The powder patterns of heated

Table 3. X-ray powder patterns of heated kobeites, stabilized cubic zirconia and heated euxenite.

	1.		2.		3.		4.		5.		6.	
hkl	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*	*d*(Å)	*I*
											7.30	1
											5.16	2
					4.14	1	4.15	1			3.66	3
					3.76	1					3.36	3
111	2.92	10	2.91	10	2.89	10	2.90	10	2.93	s	2.98	10
											2.77	2
											2.61	.3
											2.58	2
200	2.52	3	2.52	3	2.506	4	2.514	5	2.54	m	2.54	.5
											2.43	3
											2.30	1
											2.252	.3
											2.199	1
											2.182	1
											2.106	2
											2.071	.3
											2.025	.5
											1.970	.5
											1.935	1
											1.889	2
220	1.792	3b	1.779	3	1.776	8	1.778	8	1.80	s	1.823	4
											1.769	3
											1.723	4
											1.679	.5
											1.635	3
											1.605	1
											1.583	.5
											1.560	1
311	1.527	2b	1.519	2	1.514	7	1.517	7	1.53	s	1.522	.3
											1.501	.3
											1.487	4
222	1.458	1b	1.454	½b	1.452	1	1.451	1	1.467	w	1.457	1
a	5.057Å.		5.037Å.		*5.026Å.		5.029Å.		5.082Å.		a_0= 5.520Å.	
											b_0=14.57	
											c_0= 5.166	

1. Kobeite, Ushio mine, Ômiya, Kyoto Prefecture. Heated at about 900°C. in air for one hour (Cu/Ni radiation). b=broad.
2. Kobeite, Shiraishi pegmatite, Kyoto Prefecture. Heated at about 900°C. in air for one hour (Cu/Ni radiation). b=broad.
3. Kobeite, Shiraishi pegmatite, Kyoto Prefecture. Heated at about 620°C. in air for one hour. After Hutton[6] (Cu/Ni radiation). * This value is obtained by the writers after Hutton's calculation method.
4. Kobeite, Paringa River, New Zealand. Heated at about 620°C. in air for one hour. After Hutton[6] (Cu/Ni radiation).
5. Cubic zirconia stabilized by 13.8 mole % of magnesia. After Duwez and Odell[8] (Cu/Ni radiation). The original values are given in kX unit. s=strong. m=medium. w=weak.
6. Euxenite, Ontario, Canada. Heated to 1000°C. After Arnott[1] (Cu/Ni radiation).

materials studied by the writers are indexed in the same manner and the cell constants are calculated as 5.057Å. for the Ushio Mineral and 5.037Å. for the Shiraishi kobeite. Both of them are close to magnesia-stabilized zirconia (Column 5)[3] in spacings. In Table 3, the X-ray powder pattern of heated euxenite[1] (Column 6) is also listed to show the difference from that of kobeite.

As stated by Komkov[7], heating a metamict mineral generally results in the production of a mixture of oxides of the constituent elements of the mineral. In case of kobeite it is plausible that the heat treatment has produced cubic or pseudocubic zirconia stabilized by the available oxide components in kobeite such as CaO, MgO, MnO etc.[4,9], which have the ability to stabilize zirconia into cubic state. Since the diffraction peaks of the kobeites obtained by the writers are rather broad especially in the higher angle region, the question of symmetry of the product is still open.

Discussion

The specimens of kobeite from the original locality that was used in this study have the same crystal habit and mode of occurrence as those originally described by Takubo and others[12]. The X-ray powder patterns of heated material closely agree with that obtained by Hutton[6] who studied the kobeite from the original locality designated by Minato, one of the original authors. Thus the identity between the Shiraishi kobeite and the original specimen is not ambiguous.

Among multiple oxide minerals hitherto known[8,10], titanium and zirconium rich species are zirkelite, an unnamed mineral in Dana's System of Mineralogy, 7th Ed., Vol. 1[8], polymignyte and zirconolite[2]. But all of them are different from kobeite in chemical composition. Hutton[6] suggested that kobeite is a distinct and valid mineral species belonging to multiple oxides according to the X-ray powder patterns of heated materials. The results obtained by the writers not only agree with Hutton's opinion but also support it with chemical criteria.

In conclusion, the writers are inclined to recognize kobeite as a

distinct mineral species belonging to multiple oxides rich in titanium, zirconium and yttrium group rare earths.

Acknowledgement

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COSALITE FROM THE HAGIDAIRA MINE, GUN'MA PREFECTURE, JAPAN

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Abstract

A new mode of occurrence of cosalite from Japan and its mineralogical properties are described. The mineral was identified by X-ray studies and chemical analyses. It occurs in a bedded type manganese deposit in a Palaeozoic formation. Acicular crystals were found in a vug of rhodonite with quartz or growing on the surface of quartz crystals. The cosalite is associated with such metallic minerals as gersdorffite, niccolite, huebnerite, scheelite, sphalerite, galena, pyrrhotite, uraninite, etc., as well as manganese minerals.

X-ray and crystallographic data, optical properties, etch tests and chemical analysis are presented. Cell constants: $a_0=19.09$Å., $b_0=23.89$Å. and $c_0=4.058$Å. Space group: D_{2h}^{16}-Pbnm.

Introduction

During a geologic reconnaissance for radioactive anomaly in the Ashio mountainlands in the autumn of 1958, some manganese ore deposits in the Palaeozoic formation were surveyed. At the Hagidaira mine, Gun'ma Prefecture, the author found a metallic mineral of hair-like flexible crystal similar to boulangerite or jamesonite, associated with rhodonite and quartz. The mine is located 13 km. southwest of the Ashio mine, one of the leading copper mines in Japan, or 30 km. southwest of Nikko (Fig. 1).

The mineral has been identified as cosalite [$Pb_2Bi_2S_5$][4) 10) 12)], by X-ray studies and chemical analyses. This is the first occurrence of cosalite in Japan. It is noteworthy that the cosalite from the Hagidaira mine offers a new mode of occurrence of the mineral and that it will

present a more accurate crystllographic data[5] than ever described due to its well developed crystals.

In this paper the author wishes to present a brief explanation of the new occurrence and mineralogical properties of the cosalite.

Fig. 1. Index map showing the location of the Hagidaira mine, Gun'ma Prefecture.

Geology

The rocks in the mining district consist mainly of slate, sandstone, thin-bedded chert, and massive chert of Lower Permian age[11]. The rocks have been intruded and thermally metamorphosed by the Sôri granite occupying the area of 6 km. by 12 km. A distinct metamorphic aureole is recognized within the zone of about one to two kilometres from the contact. The inner zone, that is highly metamorphosed part, consits of cordierite hornfels, while the outer zone, of biotite hornfels. The Hagidaira manganese deposit is located near the marginal part of the biotite hornfels zone.

The country rocks of the manganese ore deposits consist mainly of massive and thin-bedded chert and hornfels. The geology and the manganese deposits in the district have been thoroughly studied by T. Watanabe and others[11]. The strike of the strata is, in general, N. 70°E., and dip 60°~80°N. A pegmatitic quartz vein, 30~40 cm. in thickness, is intruded along the hanging wall between the manganese ore body and the host rocks (Fig. 2).

Ore deposits

The deposits of the Hagidaira mine[9] belong to the typical bedded manganese deposit occurring peneconcordantly[3] in the chert-rich zone

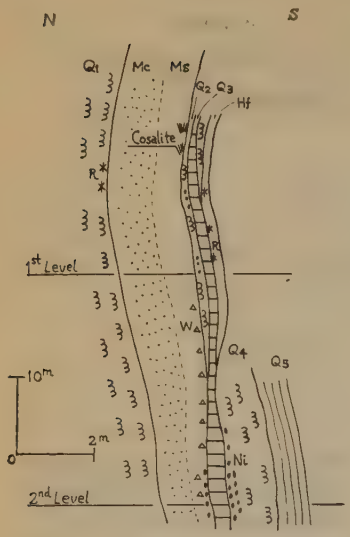

Fig. 2. Schematic cross section of the manganese ore body with cosalite.

Q_1: Massive chert containing small amounts of racioactive minerals (R).

Mc: Manganese ore mainly composed of manganese carbonate ore (Tan-man-kô), containing small amounts of manganosite.

Ms: Manganese ore mainly composed of manganese silicate ore (Kei-man-kô), characterized by small amounts of cosalite, and tungsten and nickel minerals (W and Ni).

Q_2: Massive chert of the hanging wall.

Q_3: Pegmatitic quartz vein intruded into manganese ore.

Hf: Pelitic hornfels of the hanging wall containing radioactive minerals (R).

Q_4: Massive chert of the hanging wall characterized by the presence of gersdorffite and niccolite.

Q_5: Thin-bedded chert of the hanging wall.

of the Palaeozoic terrain in Japan. More than two hundred manganese deposits of this type have been discovered in the Ashio mountainlands[11]. The Kaso mine, famous for its complex mineral paragenesis[13], is 26 km. to the east of the mine.

The manganese ore bodies together with country rocks have been folded due to granite intrusion, and form a sharp syncline plunging about 45° to the east. So far as the deposits have been developed, the dimension is about 50 m. in strike length, about 100 m. in dip length, and about one to three metres in thickness. The ores on the foot wall side are mainly composed of manganese carbonates (Tan-man-kô), while those on the hanging wall side, of manganese silicates (Keiman-kô) (Fig. 2). Main ore minerals are rhodochrosite, tephroite, rhodonite, alabandite and manganosite.

Some metallic minerals strange to bedded manganese deposits have been found, and they are considered as related to the intrusion of the pegmatitic quartz vein. They are *cosalite*, huebnerite[6], *scheelite*,

sphalerite, galena, pyrrhotite, *gersdorffite*, *niccolite*, *uraninite* and others. Italicized minerals are recognized by the author for the first time. A paragenesis of cosalite and huebnerite has been described by H. Bancroft[1].

Gersdorffite and niccolite have been found disseminated on the hanging wall side of the manganese silicate zone and/or metamorphosed massive chert (Q_2, Q_1 in Fig. 2) closely associated with spessartine, sericite and quartz. The rectangular section of the gersdorffite crystal is over 10 mm. Niccolite (2~3 mm. in diameter) often occupies central part of the gersdorffite aggregates. Uraninite is found in hornfels associated with gersdorffite and spessartine. Uraniferous minerals are also found in vugs rich in sericite.

Occurrence of cosalite

Cosalite occurs at the upper part of the manganese silicate zone. It grows either on the surface of quartz crystals or as radial ag-

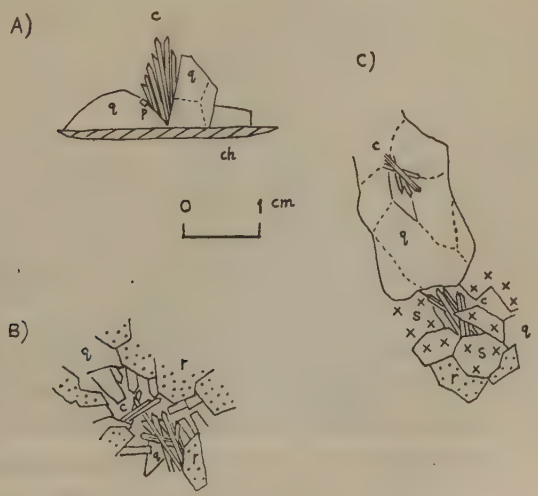

Fig. 3. Typical occurrences of cosalite from the Hagidaira mine.
c : cosalite, ch : chert, p : pyrite,
q : quartz, r : rhodonite, s : sphalerite.

gregates in vugs, 10~20 mm. in diamater, of rhodonite and quartz, sometimes surrounded by flaky rhodochrosite. Typical occurrences are shown in Fig. 3 and Fig. 4, Plate I. Since cosalite crystal is rather flexible, it was not easy to pick up well-formed crystals without distortion.

X-ray studies

On the basis of the Weissenberg photograph (Fig. 5, Plate I) of an undistorted crystal of the cosalite, the space group and unit cell constants were determined through the courtesy of Y. Takano. The results are listed in Table 1, and they are in good agreement with those obtained by L. G. Berry[2].

Table 1. Crystallographic data for cosalite.

Locality	Hagidaira mine	McElroy***
Space group*	D_{2h}^{16}—Pbnm	D_{2h}^{16}—Pbnm
Unit cell constants* a_0	19.09Å.	19.07Å.
Unit cell constants* b_0	23.89Å.	23.86Å.
Unit cell constants* c_0	4.058Å.	4.06Å.
Axial ratio	0.7978 : 1 : 0.1697	
„ (morphological)**	0.7981 : 1 : 0.1695	

* After Y. Takano.
** After Y. Takano, S. Hayashi and K. Nagashima[8].
*** After L. G. Berry[2].

Cosalite gives sharp powder lines with X-ray diffractometer, and they are measured as in Table 2.

Some crystals of cosalite from the Hagidaira mine display many excellent crystal faces, which have been measured with a two circle goniometer[8]. The axial ratio obtained from the morphological study is practically identical to that from the X-ray study, as obvious in Table 1.

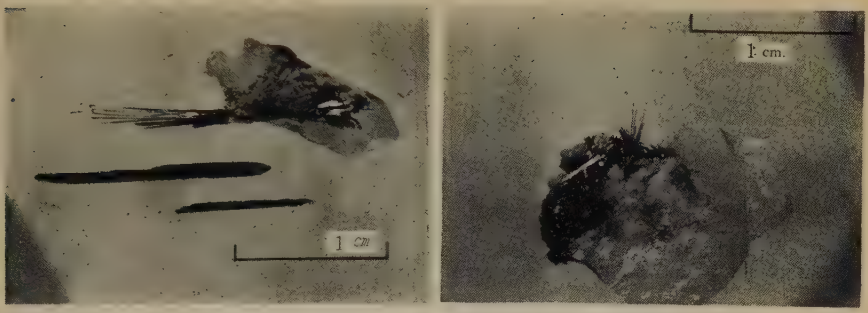

Fig. 4. Single crystals of cosalite (left) and fibrous crystals growing on the surface of quartz crystals (rigt), from the Hagidaira mine.

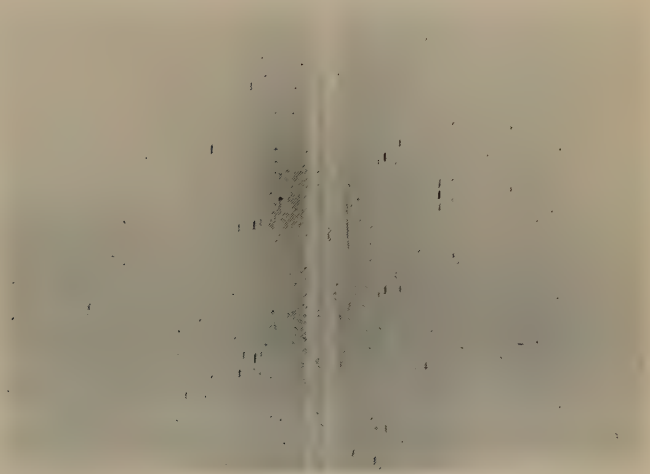

Fig. 5. Zero-level Weissenberg photograph around the c-axis of the cosalite from the Hagidaira mine.

Table 2. X-ray diffraction lines for cosalite.

hkl	1						2	
	$d_{obs.}$(Å)	I	$Q_{obs.}$	$Q_{cal.}$	$\Delta Q\times10^4$	$d_{cal.}$(Å)	d(Å)	I
230	6.15	8	.0264	.0266	+ 2	6.13		
310	5.64	9	.0314	.0316	+ 2	5.62		
420	4.45	10	.0505	.0508	+ 3	4.43		
430	4.10	12	.0595	.0595	0	4.10		
101	3.96	11	.0638	.0635	− 3	3.97		
111	3.88	11	.0664	.0652	−12	3.91		
500	3.81	8	.0689	.0686	− 3	3.81		
201	3.72	14	.0723	.0717	− 6	3.73	3.75	4
440				.0717	− 6			
031	3.64	12	.0755	.0764	+ 9	3.62	3.52	4
301	3.44	100	.0845	.0854	+ 9	3.42	3.40	10
331	3.37	23	.0881	.0872	− 9	3.38	3.30	4
231				.0874	− 7			
321	3.29	6	.0924	.0924	0	3.29		
270	3.20	6	.0977	.0962	−15	3.22		
411				.0964	−13			
401	3.08	9	.1054	.1046	− 8	3.09	3.06	—
341	2.96	22	.1141	.1132	− 9	2.97	2.95	10
161	2.81	30	.1266	.1261	− 5	2.82	2.80	6
521	2.71	5	.1362	.1363	+ 1	2.71		
670	2.66	5	.1413	.1410	− 3	2.66		
820	2.34	2	.1826	.1826	0	2.34		
281				.1830	+ 4			
830	2.29	10	.1907	.1913	+ 6	2.29	2.27	4
651	2.27	6	.1941	.1943	+ 2	2.27		
091	2.23	9	.2011	.2016	+ 5	2.23		
291	2.17	4	.2124	.2125	+ 1	2.17		
2.11.0	2.13	15	.2204	.2214	+10	2.12	2.14	6
661	2.09	3	.2289	.2291	+ 2	2.09		
860	2.05	6	.2380	.2382	+ 2	2.05		
581	2.04	11	.2403	.2406	+ 3	2.04	2.02	8
761	1.970	5	.2577	.2578	+ 1	1.970		
851	1.941	9	.2654	.2642	−12	1.946		
1.11.0	1.911	17	.2738	.2740	+ 2	1.910	1.91	4
5.10.1	1.817	6	.3029	.3032	+ 3	1.816		
162	1.799	11	.3090	.3083	− 7	1.801	1.80	4
10.5.0	1.774	7	.3178	.3179	+ 1	1.774		
532	1.748	6	.3273	.3272	− 1	1.748		
10.0.1	1.728	11	.3349	.3351	+ 2	1.728	1.75	4
10.6.0	1.722	10	.3372	.3370	− 2	1.722		
10.7.0	1.669	6	.3590	.3596	+ 6	1.668		
292	1.592	3	.3946	.3947	+ 1	1.592		
6.12.1	1.548	3	.4173	.4169	− 4	1.549		

1. Cosalite from the Hagidaira mine. Measured with a "Geigerflex" diffractometer. Cu/Ni, λ=1.5405Å, 35 kV., 15 mA. Calibrated by quartz.
2. Cosalite, ASTM card 2-0707. λ=0.709Å (Mo).

Microscopic observation

Opaque with metallic lustre. Colour, lead grey, and streak, black. Under the reflecting microscope, galena white in colour with very weak pleochroism and strong anisotropism, light grey to dark purplish grey.

Etch tests gave the following results:

HNO_3(1 : 1), quickly gives iridescent stain which spreads over area, and finally leaves pale brown and blue staining.
$FeCl_3$(20%) stains slightly pale brownish.
HCl (1 : 1), KOH (40%), KCN(20%), $HgCl_2$ (5%), negative.

These etch tests agree well with those given for cosalite by M. N. Short[7].

Chemical composition

X-ray spectrochemical analysis was carried out by the author before the chemical analysis, and it revealed that the mineral contains nearly equal amounts of lead and bismuth, and small amounts of silver, iron, manganese and copper.

Chemical analysis was kindly carried out by K. Nagashima on about 5 mg. hand-picked material. The results obtained were Pb 41% (±2%), Bi 43% (±2%), S 16% (±0.5%), Ag<1%, Fe<1%, Mn<1%. Lead and bismuth were analysed by polarographic method on the material of about 1 mg. Sulphur was analysed by microgravimetric method on about 2 mg., and iron, manganese and silver were detected colorimetrically.

It was not easy with such a small quantity of material to complete the analyses of all the trace elements such as copper and silver which may be present in cosalite. Nevertheless the result coincided well with the empirical formula $Pb_2Bi_2S_5$ (Pb 41.75%, Bi 42.10%, and S 16.15%).

Specific gravity measured with a Berman microbalance on about 1 mg. single crystal is 6.86~6.99, while the calculated value is 6.86.

Acknowledgements

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THE MINERALS OF THE NODA-TAMAGAWA MINE, IWATÉ PREFECTURE, JAPAN

III. Yoshimuraite, a New Barium-Titanium-Manganese Silicate Mineral

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Abstract

Yoshimuraite, a new barium-titanium-manganese complex silicate mineral, was found in an alkali-pegmatitic facies bordering the bedded manganese deposit of the Misago ore body of the Noda-Tamagawa mine. Yoshimuraite occurs as dark-brownish platy to tabular crystals, or sometimes in the stellate groups embedded in coarse aggregates of barium-bearing potash-feldspar, quartz, richterite, urbanite, rhodonite etc.

It resembles lamprophyllite and astrophyllite which usually occur in alkali-pegmatites. It is orange brown in colour, brittle and has a perfect cleavage parallel to {010} and distinct cleavages on {10$\bar{1}$} and {101}. Polysynthetic twinning on {010} is common. Hardness, 4½; Sp. gr., 4.13 (obs.) and 4.21 (calc.). Triclinic, with $a_0=7.00$, $b_0=14.71$, $c_0=5.39$Å, $\alpha=93.5°$, $\beta=90.2°$, $\gamma=95.3°$, and $a:b:c=0.476:1:0.366$. Space group, P$\bar{1}$. Biaxial positive with $\alpha=1.763$, $\beta=1.777$, $\gamma=1.785$, $(+)2V=85°\sim90°$ $\rho>v$, and absorption $X<Y\leqq Z$. Optical orientation, γ' nearly parallel to c-axis, α' nearly parallel to a-axis. Pleochroism, α bright yellow, β orange-brown, γ brown.

Chemical analysis by J. Ito gave SiO_2 18.25, TiO_2 10.00, Fe_2O_3 1.32, FeO 1.47, MnO 17.64, MgO 0.56, ZnO 0.50, BaO 33.51, SrO 4.62, Na_2O 0.16, K_2O 0.03, P_2O_5 3.98, SO_3 5.40, Cl 0.41, $H_2O(\pm)$ 2.34, less for Cl 0.09, total 100.10%. The results indicate a formula of approximately X_2Y_2 (Ti, Fe) $O(Si_2O_7)[(P, S)O_4]$ (OH) or X_2Y_2 (Ti, Fe) $(SiO_4)_2[(P, S)O_4]$ (OH), where X=Ba, Sr and Na, Y=Mn, Fe, Mg and Zn.

The mineral is named after Professor Toyofumi Yoshimura who has contributed much to the study of manganese minerals in Japan.

Introduction

In 1953, in the course of his investigation on manganese ores from the Misago ore body of the Noda-Tamagawa mine, the senior author (T. W.) discovered a platy brown mineral in peculiar alkali-pegmatites consisting mainly of barium-bearing potash-feldspar, quartz, richterite, urbanite and rhodonite (Plate V, Fig. 3). The mineral resembles astrophyllite in appearance but has distinctive chemical and physical properties and has been determined as a new species, a complex silicate of barium, titanium and manganese. Long after the discovery of this mineral at Noda-Tamagawa in 1953, a similar mineral was discovered by F. Hirowatari in 1959 in the Taguchi mine, Aichi Prefecture. X-ray studies of the former mineral had been carried out by the late Dr. H. Mori of our Mineralogical Institute, but discontinued because of his death in 1954. Owing partly to this sad event the completion of the present study has greatly been delayed. Later on one of the authors (Y. T.) took over the X-ray studies of that mineral and obtained the results which will be given in the following section. The name, yoshimuraite, is given in honour of Professor Toyofumi Yoshimura at the Kyushu University, who first studied in early 1930's the manganese minerals from the Noda-Tamagawa mine and has greatly contributed to the study of manganese minerals in Japan.

In this paper a brief description of the new mineral is given and, with the description of the yoshimuraite from the Taguchi mine, it will be discussed in detail in a future paper of this journal.

Occurrence and paragenesis

On the foot-wall side of the manganese ore zone of the Noda-Tamagawa mine there occurs occasionally a dark grey massive hornfels containing manganiferous minerals such as manganophyllite, richterite and urbanite. In many places along the boundary between the manganese ore and this hornfels, very coarse-grained pegmatitic

rocks with peculiar mineral paragenesis have been found. As shown in Fig. 1, the pegmatitic rocks often cut the layered manganese ore-

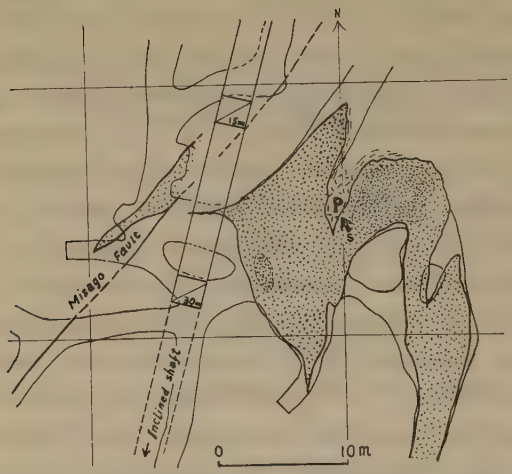


Fig. 1. Underground map showing the Misago ore body (dotted) at 30 m. Level of the Noda-Tamagawa mine, and the location of yoshimuraite-bearing alkali-pegmatite (P). Arrow (S) indicates the position of the sketch shown in Fig. 2.

bodies consisting of tephroite, rhodonite, braunite, hausmannite and other manganese minerals. The development of zoned manganese skarns along the boundaries between the pegmatitic facies and manganese ore-bodies is commonly observed as following;

quartzite or manganiferous hornfels	yoshimuraite-bearing alkali-pegmatite 1~2 m	rhodonite 1~10cm	tephroite 1~30cm	braunite ore or hausmannite-pyrochroite ore

The yoshimuraite occurs in blade or in mica-like form with length up to 5 cm. in the alkali-pegmatite facies which is found in the folded zone of the Misago ore body at 150 m. Level and is embedded in potash-feldspar, quartz, rhodonite, urbanite, richterite etc.

Only one well-formed crystal of yoshimuraite has hitherto been separated from a specimen of the Taguchi mine. The study of

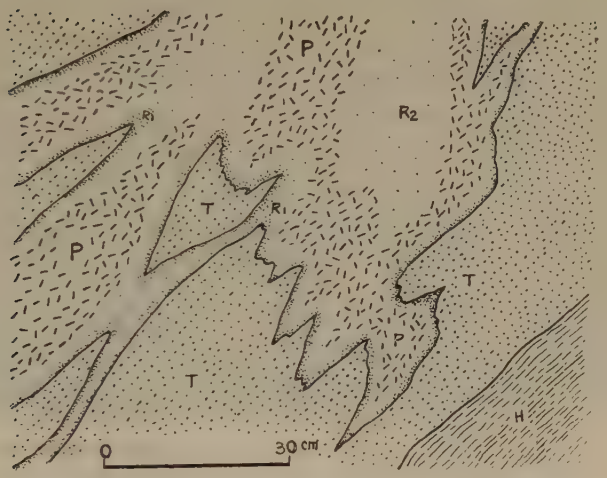


Fig. 2. Diagrammatic sketch representing development of zoned manganese-skarn around yoshimuraite-bearing alkali-pegmatite. P: alkali-pegmatite consisting of barium-potash-feldspar, quartz, urbanite, richterite, yoshimuraite, etc. T: tephroite ore. R_1: rhodonite-rim surrounding the tephroite ore. R_2: rhodonite-rich part in the alkali-pegmatite. H: manganiferous hornfels.

the relation between its crystal form and optical properties is now under way.

Physical properties

The hardness of yoshimuraite is $4\frac{1}{2}$ on Moh's scale. Measurements of specific gravity by pycnometer method gave a value of 4.13. Refractive indices measured by immersion method are α 1.763, β 1.777, γ 1.785; $(+)2V=85°\sim90°$, $\rho>\upsilon$. The pleochroic scheme is as follows: α bright yellow, β orangebrown, γ brown with absorption $X<Y\leqq Z$. Since no well-formed crystal has been found from Noda-Tamagawa, the optical orientation has not been accurately determined.

X-ray studies

The specimens suitable for X-ray experiments were made out of a lamellar single crystal. Examination of X-ray precession photo-

graphs (λ=1.5418Å.) revealed a triclinic symmetry of the crystal. Since it is most desirable to describe a lattice by a reduced cell, three shortest non coplanar translations of the lattice of yoshimuraite were chosen, and their periods which were measured in the precession films are listed in Table 1. The longest axis being chosen as b and shortest one c, the index of the perfect cleavage plane corresponds to {010} (Plate V, Fig. 4 (a)) and those of distinct cleavage planes are {101} and {10$\bar{1}$}.

Table 1. Crystallographic data for yoshimuraite.
Symmetry : triclinic.

	a_0= 7.00±0.01Å.	a^*=14.372×10^{-2}
	b_0=14.71±0.02Å.	b^*= 6.849×10^{-2}
	c_0= 5.39±0.01Å.	c^*=18.595×10^{-2}
	α= 93.5±0.2°	α^*=86.5°
	β= 90.2±0.2°	β^*=89.5°
	γ= 95.3±0.2°	γ^*=84.7°
Unit cell volume	V=549.8Å^3	V^*=1819×10^{-6}
Space group	$P\bar{1}$	
Axial ratio	$a_0 : b_0 : c_0$=0.476 : 1 : 0.366	
Density (obs.)	4.13 g. cm^{-3}.	
(calc.)	4.21 (See text)	

In the zero level of the a-axis precession photographs, very weak and diffuse reflections were observed on the lattice rows parallel to the b^*-axis at the positions which make the period of the b^*-axis one-third (Plate V, Fig. 5). This makes one impress that the true period of the b-axis is three times of the period given by the sharp reflections. However, as shown in Fig. 6(a), these reflections occur only if $l \neq 3n$, and, in a certain lattice row parallel to b^*, they appear only either at the points $nb^*+\frac{1}{3}b^*$ or at $nb^*+\frac{2}{3}b^*$, where n is an integer. These reflections appear in higher levels of the a-axis precession photographs and in the c-axis photographs as well. In these cases, positions of the reflections show slight deviations from the above particular positions in the reciprocal space. It is then suspected that, with the analogy to the X-ray reflections from polysynthetic-

Fig. 3. Polished hand specimen, showing the occurrence of yoshimuraite-bearing pegmatitic rock including massive tephroite ore from the Misago orebody (×½). Brown fine-grained part: tephroite ore, pinkish rim surrounding tephroite ore: rhodonite, coarse-grained part: alkali-pegmatitic rock.

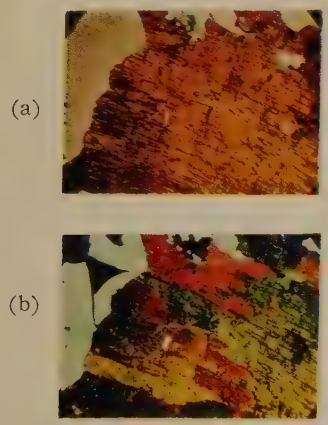


Fig. 4. Photomicrograph of yoshimuraite from the Noda-Tamagawa Mine (×12).
(a) Polarizer only, showing cleavage parallel to {010}.
(b) Crossed nicols, showing polysynthetic twinning on {010}.

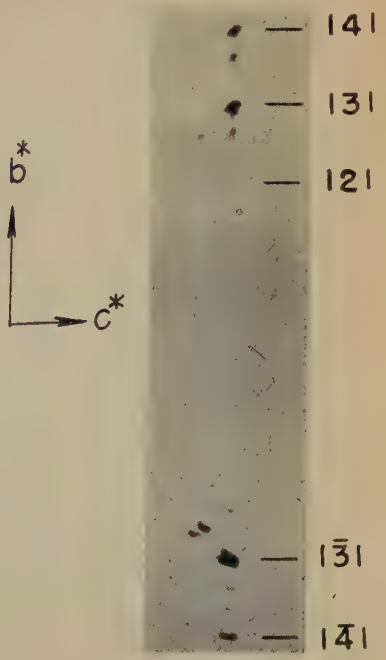
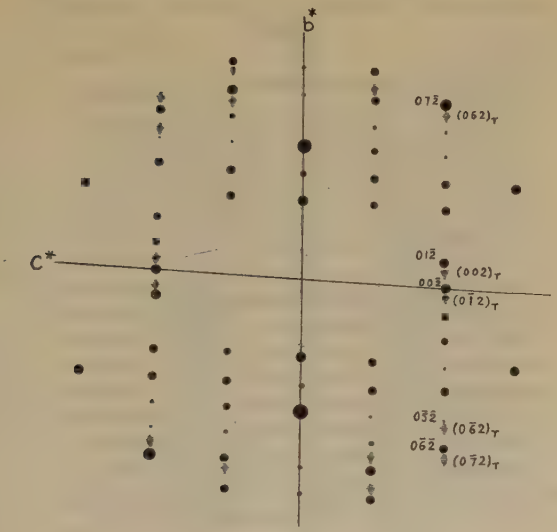


Fig. 5. Part of the a-axis, zero-level precession photograph of yoshimuraite, showing diffuse extra reflections.



(a)

Fig. 6(a). Diffraction spots observed in the Buerger precession of yoshimuraite; a-axis, zero-level. Diffuse spots are indicated by shading.

ally twinned micas[2], polysynthetic twinning occurs in yoshimuraite crystals as schematically shown in Fig. 7. Actually, under the microscope polysynthetic twinning on {010} is observed as illustrated in Plate V, Fig. 4(b).

As the matter of fact, in the reciprocal space, the following dimensional specialization exists in the lattice constants of yoshimuraite :

$$6c^* \cos \alpha^* = b^*$$

Similar relation is also approximately held among a^*, γ^* and b^*. Therefore, the twinning about the b^*-axis, with a rotation 180°, will result in giving the composite reciprocal net as shown in Fig. 6(b). If the volumes of the twin-individuals in the twin-orientation are small, the intensities of X-ray reflections from these twin-individuals should be weak and in this way the weak extra reflections of yoshimuraite may be explained as the results of polysynthetic twinning.

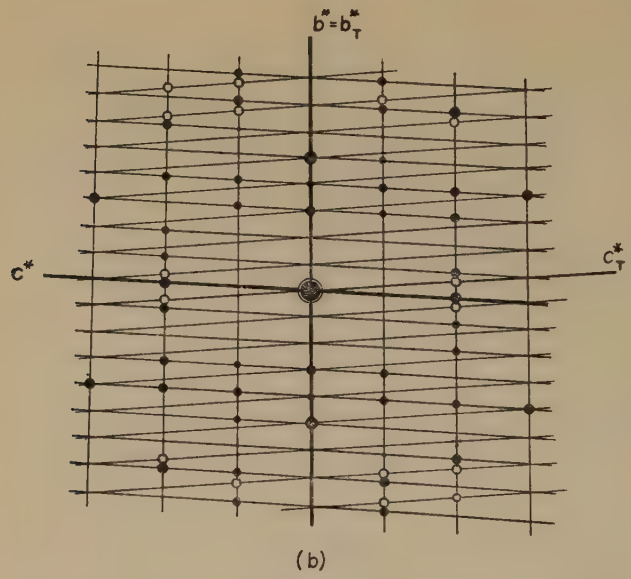


Fig. 6(b). Composite 0*kl* reciprocal net of twinned yoshimuraite. Open circles belong to the reciprocal net in twin-orientation and correspond to the diffuse spots in (a).

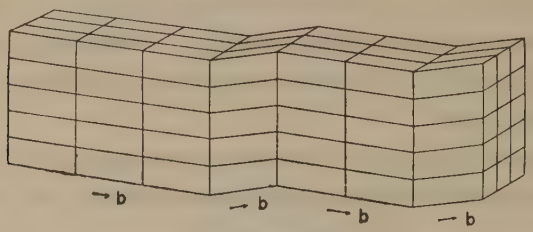


Fig. 7. Schematic representation of polysynthetic twinning of yoshimuraite.

Piezoelectric tests along approximately the three crystallographic axes of the crystal were made on an apparatus built by Iitaka[1] with negative results. If the crystals are noncentrosymmetric, the direction of the *b**-axis must be polar even with the polysynthetic twinning. Accordingly, the negative results strongly suggest the centrosymmetric space group P$\bar{1}$.

Table 2. X-ray powder data for yoshimuraite.

Measured†		Calculated††	
I	*d*	*d*	*hkl*
1	14.8	14.6	010
6	4.90	4.95	011
2	4.28	4.28	$\bar{1}01$
2	4.22	4.23	101
		4.21	021
4	4.11	4.11	$\bar{1}11$
		4.09	$\bar{1}11$
3	3.99	3.96	111
3	3.71	3.73	0 1
2	3.45	3.46	210
10	3.40	3.38	$1\bar{3}1$
2	3.34	3.36	$1\bar{1}0$
		3.32	210
6	3.24	3.22	$\bar{1}30$
4	3.13	3.12	140
4	3.05	3.04	131
10	2.94	2.94	041
		2.94	$\bar{2}01$
2	2.88	2.88	211
6	2.78	2.77	$\bar{3}21$
		2.77	$\bar{1}41$
4	2.71	2.71	002
2	2.65	2.65	$2\bar{1}0$
2	2.62	2.61	012
2	2.42	2.42	231
3	2.24	2.24	$\bar{2}41$
2	2.17	2.17	061
2	2.15	2.15	132
2	2.13	2.13	$2\bar{1}2$
		2.12	301
		2.12	$\bar{1}61$
3	2.11	2.11	$\bar{2}12$
		2.11	$\bar{1}61$
2	2.10	2.10	$\bar{1}42$
		2.10	$2\bar{2}2$
2	2.07	2.07	212
2	2.06	2.06	$\bar{2}22$
1	2.03	2.03	$3\bar{3}1$
1	1.992	1.991	$1\bar{5}2$
1	1.649	1.649	033
		1.649	$0\bar{4}3$
		1.650	$3\bar{4}2$
2	1.595	1.596	$4\bar{2}1$
		1.595	213

† Cu$K\alpha$=1.5418Å.

†† Based on: $a^*=14.372\times10^{-2}$, $b^*=6.849\times10^{-2}$, $c^*=18.595\times10^{-2}$, $\alpha^*=86.5°$, $\beta^*=89.5°$, $\gamma^*=84.7°$.

Table 2 shows the X-ray powder data of yoshimuraite which were obtained by the use of a Norelco diffractometer only for indexing powder peaks by the above lattice constants.

Chemical composition

Spectroscopic analyses of yoshimuraite yield to show the presence of Mg and Zn in addition to the major components Si, P, Mn, Ba, Fe, Ti and Sr. The result of a total chemical analysis is given in the first column of Table 4.

Method of chemical analysis for main elements in yoshimuraite is given schematically in Table 3. Alkalies were determined by flame photometric method after the separation of most of interfering elements with NH_4OH and $(NH_4)_2CO_3$. Chlorine was determined gravimetrically as AgCl after the decomposition with Na_2CO_3 fusion.

From the cell volume and observed density, the molecular weight of the cell contents was calculated to be 1367.5. Based on this value and the results of chemical analysis the chemical formula of yoshimuraite can readily be derived. Account then was made of the total number of each kind of atom in the cell. In determining chemical formula, we must take into account the requirement of space groups, and resultant chemical formula must give the calculated density in reasonable accord with the observed one. Since atoms in the tetrahedral coordination can not lie on the centre of symmetry, number of Si and that of P(S) in the cell with space group $P\bar{1}$ must be even. As seen in Table 4, number of Si in the cell is close enough to four, while that of P+S is 1.68 and much less than two. However, it may be reasonable to assume that there are two of these atoms in the cell. OH groups are, for their polarity, usually not located on the centres of symmetry and it is found that the most reasonable number of the OH groups which is conformable with the results of the chemi-

Table 3. Procedure for chemical analysis of yoshimuraite.

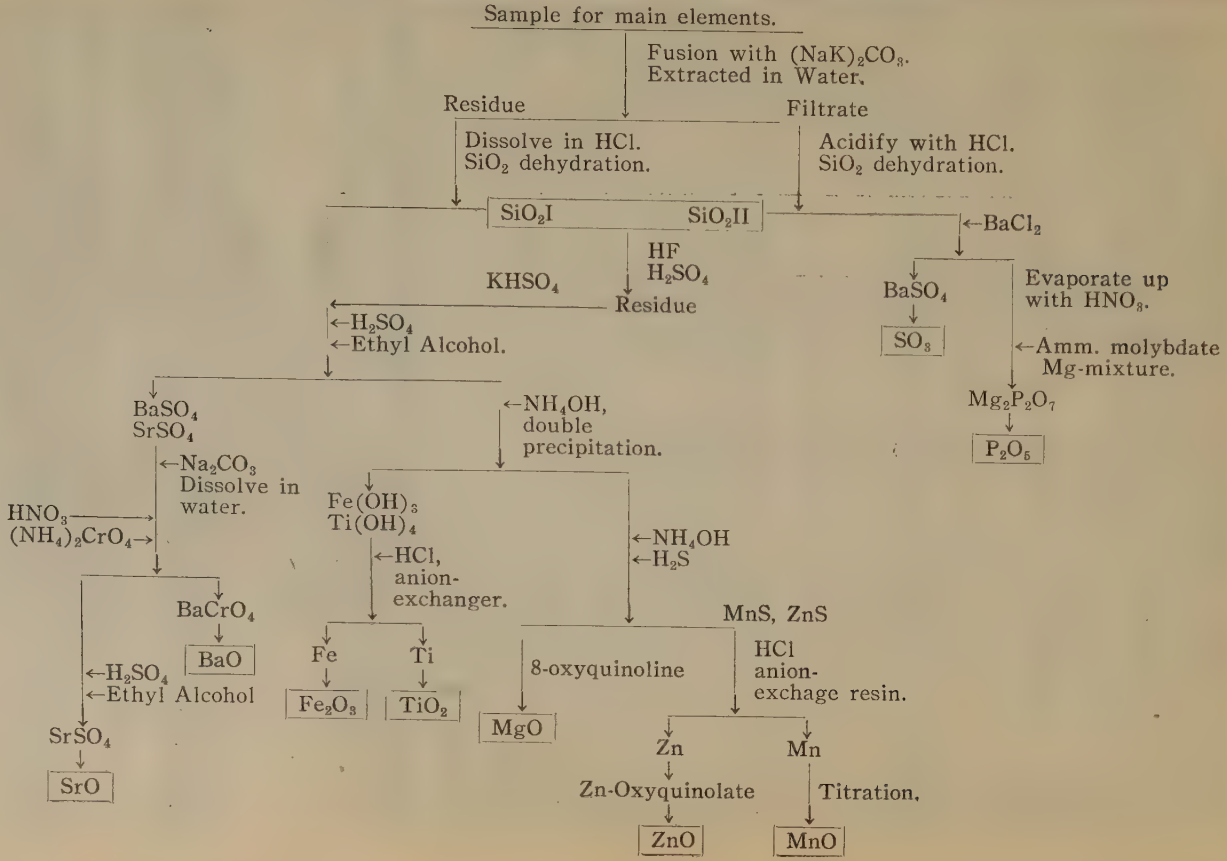


Table 4. Chemical composition of yoshimuraite.

	Wt. %	No. of oxides and Cl per unit cell	Metal atoms per unit cell		Oxygens and Cl per unit cell
SiO_2	18.25%	4.17	4.17		8.34
TiO_2	10.00	1.70	1.70	1.92	3.40
Fe_2O_3	1.32	0.11	0.22		0.33
FeO	1.47	0.28	0.28	3.95	0.28
MnO	17.64	3.40	3.40		3.40
MgO	0.56	0.19	0.19		0.19
ZnO	0.50	0.08	0.08		0.08
BaO	33.51	2.99	2.99	3.68	2.99
SrO	4.62	0.61	0.61		0.61
Na_2O	0.16	0.04	0.08		0.04
K_2O	0.03	0.00	0.00		0.00
P_2O_5	3.98	0.38	0.76		1.90
SO_3	5.40	0.92	0.92		2.76
Cl	0.41	0.16			0.16
$H_2O(\pm)$	2.34	1.37	2.74		1.37
−Cl	−0.09				
Total	100.10%				25.85
Sp. gr.	4.13				

Analyst, J. Ito (1958).

cal analysis is two*. Thus, the ideal chemical formula of yoshimuraite may well be expressed by

$$X_2Y_2(Ti, Fe)O(Si_2O_7)[(P, S)O_4](OH)$$

where X=Ba, Sr and Na,

Y=Mn, Fe, Mg and Zn.

There are two formula units in the cell. If we accept that the total number of Ti in the cell is 1.7 as given by the chemical analysis and

* Previously, a chemical formula,

$$(Ba, Sr)_4Mn_4Ti_2(SiO_4)_4[(P, S)O_4]_2(OH, Cl_3),$$

was tentatively assigned to yoshimuraite and described[3]. However, it is not likely that there are three (OH) groups in the cell from the view point of the space group requirement and the above formula should be withdrawn.

the ratio of P/S is unity, the ideal formula gives the calculated density 4.21 g. cm.$^{-3}$ which is in good agreement with the observed value 4.13 g. cm.$^{-3}$. The ideal formula is fully supported by the chemical composition of yoshimuraite which was later found from the Taguchi mine.

The chemical formula of yoshimuraite can also be given in the form of an orthosilicate,

$$X_2Y_2(Ti, Fe)(SiO_4)_2[(P, S)O_4](OH),$$

but accurate expression of the formula should await the completion of the structure analysis.

Acknowledgements

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MINERALOGICAL ABSTRACTS

FROM

THE SCIENTIFIC PAPERS PUBLISHED

IN JAPAN

Apparatus and techniques: 3038, clay minerals: 3039–3042,
economic minerals and ore deposits: 3043–3044,
experimental mineralogy: 3045–3058, mineral data: 3059–3066,
physical properties of minerals: 3067,
rock-forming minerals and petrology: 3068–3072,
various topics: 3073–3075.

Apparatus and Techniques

3038. **Iitaka (Yoichi) and Sakurai (Toshio):** *The crystallographic calculation by the parametron computer P. C. 1.* Kobutsugaku Zasshi, **4**, 409–434, 8 figs. (1960). (in Japanese)

The use of the Parametron Computer P. C. 1 for the crystallographic calculation is described. Programmes have been devised for the corrections of Lorentz-polarization factors, transform between direct and reciprocal lattices and calculation of Q-values, 2θ and $\sin\theta/\lambda$. The computer can be used extensively for calculations needed in the determination and refinement of crystal structures, i. e. programmes are given for the calculation of structure factors, the computation of two-dimensional Fourier synthesis, correction of the temperature factors, the computation of differential Fourier synthesis, least squares and molecular transform and the calculation of atomic distance. These programmes are listed in a table.

Clay Minerals

3039. **Shirozu (Haruo):** *Ionic substitution in iron-magnesium chlorites.* Mem. Fac. Sci., Kyushu Univ., Ser. D, **9**, No. 3, 183–186, 1 fig. (1960).

Studies on the chemical composition of well-crystallized chlorites of iron-magnesium series revealed the followings: Substitution of Al^{3+} for Si^{4+} (and Mg^{2+} or Fe^{2+}) is limited to a considerably narrow range, and there is a general trend from magnesium chlorites to iron chlorites that the aluminum content is greater in the latter than in the former; The number of Al in the four tetrahedral (Si, Al) sites ranges from 1.0 to 1.3 for nearly all of magnesium chlorites, and from 1.3 to 1.5 for iron chlorites. These results are discussed from the view point of structural chemistry.

3040. **Mitsuda (Takeshi):** *On acid clays and cristobalite from Itoigawa.* Kobutsugaku Zasshi, **4**, 335-362 (1960). (in Japanese)

X-ray powder patterns, differential thermal curves, ignition losses, chemical constituents, base-exchange capacities, infra-red absorptions, and electron micrographs were examined for various acid clays from Itoigawa, with the result that montmorillonite, cristobalite, and gelatinous silicic acid were found to be the main constituents of these clays. Hydrated halloysite was also found at the margin of ore body. An irregular mixed-layer mineral consisting of kaolinite and montmorillonite layers was found at a contact zone between halloysite and acid clays. The amount of cristobalite became smaller at the marginal zone of the body. In fact, no cristobalite was found in halloysite clays. The author's conclusion is that montmorillonite has feen formed mainly due to hot water action and surface weathering.

3041. **Nakamura (Takeshi):** *Chlorite from the Ashio Copper Mine.* Kobutsugaku Zasshi, **4**, 383-397 (1960). (in Japanese)

Four specimens of chlorite found in vein as gangue minerals at the Ashio Mine were studied. Chemical and X-ray powder data were given. Chlorite in the Cu and Zn-Pb veins in rhyolitic body is characterized by extraordinarily high value of $Fe^{2+}/(Fe^{2+}+Mg)$, while chlorite in the altered rhyolite has relatively lower value as may be infered from the chemical composition of altered rhyolite. Characteristic features of chlorite from Cenozoic "subvolcanic" type deposits in Japan were also discussed from a view point of ore genesis.

3042. **Mitsuda (Takeshi):** *Pseudomorphs of kaolinite after biotite. (Studies on mechanism of weathering, 1st report).* Journ. Fac. Sci., Hokkaido Univ., Ser. IV, **10**, 481-494, 3 pls. 6 figs. (1960).

X-ray, thermal, chemical analyses and infra-red tests were made of pseudomorphic kaolinites after biotites from a deep-weathered granite.

(1) Crystals are of hexagonal prism and well-crystallized with the c-axes parallel to those of parent biotites, the $d(001)$ being 7.17Å. The Al/Si ratio ranges over 0.89～1.07, showing a good agreement with the theoretical value.

(2) An interpretation of the formation of the kaolinite is given that alkalis, alkali-earths and a part of iron and silicon in biotites were dissolved out by meteoric water (pH 5～6) during a long period to produce pseudomorphs of kaolinite after biotite. An assumption that the Al in biotite was not dissolved out under the condition of pH 5～6 makes it possible to calculate the volume change of crystal from biotite to kaolinite. With these assumptions, the calculation showed a good agreement with the observed value.

Economic Minerals and Ore Deposits

3043. **Takeuchi (Tsunehiko), Sugaki (Asahiko), Suzuki (Teruo) and Abe (Hiroshi):** *Ore deposits of the Ôhori mine, Yamagata Prefecture, Japan.* Mining Geol., 10, 8–28, 22 figs. (1960). (Japanese with English abstract)

Bustamite of the Ôhori mine occurs as a gangue mineral of the replacement deposit in a calcareous bed intercalated in lipalitic tuffs of Miocene age, and is intimately associated with wollastonite, rhodochrosite, epidote and garnet. Ore minerals are sphalerite, chalcopyrite, pyrite and galena. It forms radial aggregates of fibrous crystals, light grey to brownish grey in colour. Straight extinction with positive elongation. Analysis gives, SiO_2 45.65, TiO_2 0.08, Al_2O_3 1.12, Fe_2O_3 1.02, FeO 1.48, MnO 27.34, MgO 2.41, CaO 18.91, $H_2O(+)$ 1.16, $H_2O(-)$ 1.07, total 100.24%, with chemical formula, $(Ca_{0.44}Mn_{0.50}Fe_{0.03}Mg_{0.03})_{1.05}Si_{0.98}O_{3.00}$. The X-ray powder patterns are in good agreement with the previous data on bustamite.

The features of the ore deposits are described in detail.

3044. **Ishibashi (Masao):** *Au-Ag-tellurides from the Daté mine, Hokkaido, Japan.* Mem. Faculty of Eng., Hokkaido Univ., 11, 73–84, 3 figs. (1960).

Microscopic study, mainly by means of etch test, of polished specimens of gold bearing quartzose ores from the Daté mine, Hokkaido showed the presence of krennerite, hessite and petzite as Au-Ag-telluride minerals. The paragenesis of these ores and of related massive sulphide ores of "Black Ore" type of this mine and similar deposits of Japan are discussed. It is clarified that the combination of Au, Bi and Te varies according to the difference of geological environment. Under the volcanic hydrothermal condition Au and Te combination is common, while under the plutonic hydrothermal condition, Te associates with Bi rather than Au. It is interesting that the mineralization under metamorphic condition is similar to the volcanic one.

Experimental Mineralogy

3045. **Kishii (Toru):** *Crystalline materials produced by devitrification and corrosion in a melting furnace for amber glass containing MnO.* Toshiba Review, 14, 755–757 (1959).

Polarizing microscopic observations were made of both crystals produced by devitrification of black glass used for insulation of electric bulbs and the reaction products between the furnace wall and glasses. Main constituents of the glass were SiO_2, Na_2O and CaO. It also contained 5% MnO, 6% Al_2O_3, 1% PbO, 1% Fe_2O_3 and 3% K_2O by weight.

Crystals produced by devitrification were albite (aggregate of four-sided crystals), pyroxene (small prismatic crystals), devitrite (radial growth) and β-wollastonite (radial growth, plate or small prismatic crystals or four-sided tubes).

Corrosion products were corun-

dum (hexagonal plate), β-alumina (hexagonal plate), nepheline (hexagonal prism or pyramid) and spinel.

Nothing new was found in those products as compared with crystals found in usual soda-lime and soda-lime-magnesia glasses, except that their crystal habits were different from the latter ones.

3046. **Kishii (Toru)**: *Silica crystals produced by devitrification in glass melting furnaces*: Toshiba Review, **14**, 1072–1075 (1959).

Polarizing microscopic observations were made of crystals formed by devitrification of various glasses. I. Soda-lime-magnesia glass: Quartz, cristobalite and tridymite were formed together with β-wollastonite and devitrite. Quartz was of hexagonal bipyramid or prism. Some crystals were platy with Japanese twinning. Crystals of cristobalite were skeletal, dendritic, or octahedral with octahedral faces curved toward inside. Tridymite crystals were of hexagonal dendritic or platy shape. II. Lead-potash glass: Aggregates of tridymite were formed with their cross sections of lath-type. III. Ample glass: Cristobalite was produced with the development of fine cracks throughout the glass body. Tridymite was occasionally formed. IV. Boro-silica glass: Development of fine cracks due to the formation of cristobalite.

3047. **Nishimura (Jiro)**: *Synthesis of ZnS crystals by sublimation and recrystallization.* Journ. Appl. Phys. Japan, **28**, 651–656 (1959).

A method of preparing 1~10g. single crystals of ZnS is described. A polycrystalline body was prepared from powder of ZnS by the sublimation-recrystallization method. The body consisted of needle-like or prismatic crystals with faces developed in the same orientation. Then, it was heated for 60 hours in a ZnS atmosphere to produce large single crystals by grain growth. Zn/S ratio of the products was not always 1:1. Low value of S was observed for those prepared at higher temperatures. In polycrystalline body, {0001} was the growth edge in many cases; while, in the final product, faces belonging to the zone $[11\bar{2}0]$ formed the growth edge.

3048. **Kunitomi (Minoru)**: *Studies of artificial quartz.* Repts. Fac. Eng., Yamanashi Univ., **10**, Commemoration of the Tenth Anniversary of the Founding of the Faculty, 181–195 (1959).

A brief summary of the researches on synthetic quartz in the writer's laboratory in these five years is given. The method has been based on the control of temperature-gradient in the vessel. Various experimental conditions have been examined. The nature of crystal nuclei and solutions together with temperature-distribution within the vessel are discussed in connection with the physical properties of the products. Sealing methods of the vessel are also explored. Measurements are made of the piezo-electric property of the products with the result that artificial quartz has several advantages

in this property as compared with natural one.

3049. **Saito (Hajime) and Ogasawara (Ken-ichi):** *Synthesis of various types of fluo-amphibole by isomorphic substitution.* Kogyo Kagaku Zasshi, **62**, 976–978, 1 fig. (1959). (in Japanese)

Syntheses of various types of fluo-amphibole such as tremolite, richterite, arfvedsonite, edenite and riebeckite have been accomplished from mixtures of Na_2CO_3, $CaCO_3$, MgO, Fe_2O_3, Al_2O_3, MgF_2 and SiO_2. The mixtures were made in accordance with chemical compositions of the minerals, melted in crucibles, held for thirty minutes at 1350°C. and then cooled down to 1000°C. with a cooling rate of 30°C./hr. The identification of the products was made by microscopic and X-ray methods. The order of crystallinity of the products was arfvedsonite > riebeckite, richiterite > tremolite, edenite. An oxydizing atomosphere was needed for the crystallization of arfvedsonite because of the reduction of Fe^{3+}. Each of the following different methods was tried. (a) Oxygen gas was sent into the furnace. (b) Fe^{3+} was replaced by Al^{3+}. (c) $NaNO_3$, an oxydizing agent, was substituted for a part of Na_2CO_3. The method (c) showed the best result.

3050. **Kishii (Toru):** *Crystals produced by devitrification of soda-lime-magnesia glass in a melting furnace.* Toshiba Review, **15**, 61–65 (1960).

Crystals produced by devitrification of glass formed at interstices of fire-bricks of melting furnace were examined under a polarizing microscope. X-ray powder photographs were also taken when the specimens were obtained in sufficient amount. The main constituents of the glass were SiO_2, Na_2O, CaO, MgO and Al_2O_3. Other oxides were found to be less than 1% by weight. (I) Devitrite: Main constituent mineral. Radial aggregate of needle-like or fibrous crystals. Paragenesis with quartz, albite and diopside was frequently observed. (II) β-wollastonite. Radial aggregate of small prismatic crystals with occasionally four-sided prismatic or platy crystals. (III) Diopside: Pyramidal faces were well-developed. Occasionally tabular. (IV) Plagioclase: Two different types, one of which was close to albite; the other slightly rich in An component.

3051. **Kishii (Toru):** *Crystals produced by devitrification of soda-lime-magnesia glass (Part II).* Toshiba Review, **15**, 132–135 (1960). [Ref. 3046, 3050.]

A further examination of the products from the melting furnace described in the previous reports is described.

(I) Alkali-pyroxene. Aggregate of needle crystals. Greenish probably due to the presence of iron oxides. Judging by the X-ray powder photographs, it does not seem to belong to the acmite group in its chemical composition. (II) Diopside-enstatite system crystals. Similar to diopside in their appearance, but the X-ray pattern is dif-

ferent from that of diopside and resembles that of enstatite. (III) Various minute crystals. Though an attempt at identifying these crystals resulted in failure, it was confirmed that these crystals were different from those described in (I) and (II).

3052. **Naka (Shigeharu) and Noda (Tokiti):** *Supercooling and crystallization of fluor-phlogopite melt.* Kogyo Kagaku Zasshi, **63**, 777 (1960). (in Japanese)

A large single crystal was prepared by quenching the melt immediately after holding it at a slightly higher temperature than 1375°C. (melting point of the body) for a short time. Supercooling did not take place because of the residual crystal nuclei. A long holding time at a temperature higher than the melting point resulted in the difficulty of crystallization; more than 50°C. supercooling being observed. A body crystallized below 1320°C. contained chondrodite-like crystals along with fluor-phlogopite. Refractive indices of the former were similar to those of natural chondrodite. Calculation of refractive indices based on an assumption that hydroxyl ions in chondrodite were all replaced by fluorine ions resulted in a good agreement with those of the synthetic chondrodite.

3053. **Naka (Shigeharu) and Noda (Tokiti):** *Melting point and crystallization temperature of synthetic fluor-phlogopite.* Kogyo Kagaku Zasshi, **63**, 232 (1960). (in Japanese)

Measurements by means of quenching and differential thermal analysis were made of melting point and crystallization temperature of the mica with $\alpha=1.5170$, $\gamma=1.5498$, and $2V=14°$ which was synthesized by the authors. To prevent evaporation, specimens were sealed in a platinum crucible. Results from the two different methods gave 1375 ±5°C. for both the melting and crystallization temperatures. An effect of thermal history of the melt on its crystallization temperature was observed and a high crystallization temperature without supercooling was obtained only when the melt was held at a slightly higher temperature than the melting point for a short time and then quenched.

3054. **Noda (Tokiti) and Matsuoka (Hiroshi):** *Melting of carbon and graphite crystals produced.* Kogyo Kagaku Zasshi, **63**, 465 (1960). (in Japanese)

Charcoal and carbon black were melted by heating under a pressure of more than 100 atms. of argon and beads of melted carbon of 1∼3mm. in diameter were obtained. Melting point: 4020±50°K. Lattice constants of melted carbon showed $c_0=6.707\pm0.0007$Å., $a_0=2.461\pm0.0002$Å. as compared with $c_0=$ca. 6.714Å. of unmelted part. Thin small crystals of melted carbon were observed under an electron microscope.

3055. **Hayashi (Hiroshi) and Naka (Shigeru):** *Synthesis of nickel-olivine.* Repts. Government Industr. Research Inst., Nagoya, **9**, 196-201 (1960).

Nickel-olivine and olivine of

$(Ni, Mg)_2SiO_4$ system were synthesized by the following method. NiO prepared from a mixture of silica and nickel nitrate and MgO from its chloride were mixed together, fired at 1400~1500°C. in a platinum crucible. The product was ground again, shaped, and then heated at 1400~1500°C. for 1~5 hours. X-ray pattern of olivine type was obtained for the product with the chemical composition of Ni_2SiO_4. Under conditions such as low reactivity of NiO with SiO_2, low heating temperature or short heating time, free NiO and SiO_2 were observed remaining unreacted. Products from bodies of $(Ni, Mg)_2SiO_4$ system also showed X-ray patterns of olivine type, indicating the presence of continuous solid solution. Reactivity of NiO with SiO_2 was increased with increasing MgO. With SiO_2 in excess of Ni_2SiO_4, olivine and cristobalite were produced together with remaining free NiO, no enstatite being formed.

3056. **Kiriyama (Ryôiti) and Iwasaki (Hiroshi):** *Process of mineral formation from obsidian under hydrothermal conditions.* Jour. Geol. Soc. Jap., **66**, 242–250 (1960).

Hydrothermal reactions of obsidian were carried out under various chemical conditions in the temperature range 150~300°C. using Morey-type autoclaves. Obsidian with magnesia ($SiO_2 : Al_2O_3 : MgO = 8.2 : 1 : 2$) has yielded analcite and montmorillonite at 300°C. It was confirmed that the most favourable condition of analcite formation is about 250°C.

3057. **Hayashi (Akira):** *The effect of impurity and temperature on the polytipism of silicon carbide.* Kobutsugaku Zasshi, **4**, 363–371 (1960). (in Japanese)

Measurements were made of formation- and decomposition- temperatures of seven different specimens of α-SiC together with qualitative chemical analysis to clarify a bearing which impurities might have on polytypism. The main impurity was found to be aluminum. With increasing aluminum, the transformation of α-SiC follows from α-II to α-I, and from α-II to α-III (according to Thibault classification). Aluminum range of each type is presumably 0.05~0.10% for α-I, ~0.05% and 0.10~0.3% for α-II, and 0.3%~ for α-III, respectively. In colour α-I, yellow or green; α-II, light green for ~0.5% Al and green for 0.10~0.3% Al; α-III, black.

3058. **Ikeno (Teruo):** *On the transition of Fe_2O_3.* Kobutsugaku Zasshi, **4**, 435–449, 15 figs. (1960). (in Japanese)

(1) Solid reactions of α-Fe_2O_3 in air were examined by the X-ray diffraction method at high temperatures and the measurements were made of changes in the strength and volume of briquette. (2) Over the temperature range from 1000° to 1230°C., random displacements of atoms in the α-Fe_2O_3 take place, resulting in the recombination of particles by the first-step self-diffusion. (3) At 1230°C., a defect lattice is formed by partial expulsion

of oxygens in the lattice and the recombination of particles is advanced by the second-step self-diffusion. At 1395°C., the α-Fe_2O_3 lattice is transformed to the Fe_3O_4 lattice of defect type with iron atom vacancies. At this stage, the recombination is caused by the third-step diffusion.

Mineral Data

3059. **Yoshinaga (Mayumi):** *Helvite from Yagisawa Mine, Nagano Prefecture, Japan.* Mem. Fac. Sci., Kyushu Univ., Ser. D, **9**, 47–53, 1 fig. (1959).

Some new data of recently reported helvite from the Yagisawa mine (Abstract: Miner. Jour., **2**, 429) are given. Chemical analysis gives: SiO_2 31.29, Al_2O_3 0.52, TiO_2 none, BeO 13.88, MnO 47.36, FeO 4.19, ZnO none, CaO 0.17, MgO tr., S 5.93, H_2O 0.01, O=S −2.96, total 100.39%; $d_4^{23}=3.21$; $a_0=8.272$Å.; $n=1.736$. X-ray powder data of dannemorite and huebnerite (associated minerals) are also given.

3060. **Matsuda (Shunji):** *Alkali elements in beryl.* Kobutsugaku Zasshi, **4**, 398–403 (1960). (in Japanese)

Quantitative chemical analyses of Rb, Li and Na are made of beryl. Interrelation between the amount of these elements is discussed. Rb_2O increases as K_2O increases, while Li_2O is nearly constant.

3061. **Matsumoto (Yukio) and Miyahisa (Michitoshi):** *Ferrohastingsite from the Obira Mine, Kyushu, Japan.* Kobutsugaku Zasshi, **4**, 372–382 (1960). (in Japanese)

Ferrohastingsite from the Obira Mine occurs as fibrous aggregates, having a dark green colour, associated with hedenbergite, andradite and vesuvianite. H=5.5~6; sp. gr. 3.32; $\alpha=1.695$, $\beta=1.710$, $\gamma=1.713$; $(-)2V=29°$; $Z\wedge c=16.5°$; X=greenish brown, Y=olive green, Z=bluish green. Chemical analysis gave the following results: SiO_2 38.82, Al_2O_3 9.07, Fe_2O_3 5.57, FeO 25.87, MgO 1.91, CaO 11.79, Na_2O 2.79, K_2O 0.92, $H_2O(+)$ 2.31, $H_2O(-)$ 0.27, TiO_2 0.58, MnO 0.25, F 0.06, Cl 0.20, (less O for F and Cl 0.07), total 100.34%. X-ray powder patterns are identical with those of monoclinic amphiboles. Differential thermal analysis curve was compared with those obtained by Wittels. The mineral seems to have been formed in the later stage of skarn mineralization.

3062. **Kawai (Teikichi):** *Chemical studies on minerals containing rare elements from the Far East (Rep. 48) A mineral similar to ishikawaite and belonging to the samarskite series, from Iriyama, Ishikawa-machi, Fukushima Prefecture.* Nippon Kagaku Zasshi, **81**, 1049–1051 (1960). (in Japanese)

A brownish black, samarskite-like mineral was found in pegmatite at Iriyama. Sp. gr., 5.8. X-ray study shows the mineral to be metamict. After heating for about three hours, the diffraction lines similar to those of heated samarskite or euxenite, were obtained. The result of chemical analysis is as follows: MgO

0.70, CaO 0.00, MnO 1.10, FeO 12.17, $\sum Y_2O_3$ 7.21, CeO_2 0.00, ThO_2 0.00, TiO_2 0.68, SnO_2 0.00, UO_2 23.14, UO_3 5.15, $(Nb, Ta)_2O_5$ 49.35, H_2O 1.11, total 100.61%. The ratio of U/$\sum$ rare-earth elements for the mineral is larger than that for samarskite or ishikawaite, and the mineral is considered to be a uranium rich member of the samarskite-ishikawaite series.

3063. **Kawai (Teikichi):** *Chemical studies on minerals containing rare elements from the Far East (Rep. 49). Ilmenorutile from Uzuminé, Sukagawa-shi, Fukushima Prefecture.* Nippon Kagaku Zasshi, **81**, 1052 (1960). (in Japanese)

Ilmenorutile was found in pegmatite at Uzuminé, associated with monazite, samarskite and euxenite. Sp. gr., 4.3. The result of chemical analysis is as follows: MgO 2.34, CaO 1.52, MnO 15.96, FeO 19.12, Al_2O_3 5.12, TiO_2 37.10, $(Nb, Ta)_2O_5$ 15.43, SiO_2 2.27, H_2O 0.87, total 99.82. The mineral is characterized by larger contents of manganese and is considered to be a solid solution between manganomossite and rutile, a manganoilmenorutile.

3064. **Kawai (Teikichi):** *Chemical studies on minerals containing rare elements in the Far East (Rep. 50). Fergusonite-like mineral from Uzuminé, Sukagawa-shi, Fukushima Prefecture.* Nippon Kagaku Zasshi, **81**, 1053 (1960). (in Japanese)

A fergusonite-like mineral was found in pegmatite at Uzuminé. It is strongly radioactive. Sp. gr., 5.5. X-ray powder lines are slightly different from those of heated fergusonite, euxenite or samarskite. The result of chemical analysis is as follows: MgO 4.55, CaO 3.97, FeO 4.20, Al_2O_3 2.57, $\sum Y_2O_3$ 17.92, Ce_2O_3 0.40, ThO_2 1.44, SnO_2 etc. 0.43, TiO_2 7.83, UO_2 11.46, UO_3 0.53, $(Nb, Ta)_2O_5$ 41.76, SiO_2 1.69, H_2O 2.07, total 100.82%.

The distribution of lantanid elements belongs to the thalenite type. Assuming that the uranium comes from the uraninite inclusion, the chemical formula of the mineral was determined as $ABO_{3\cdot4}$. It is considered to be a titaniferous fergusonite.

3065. **Kawai (Teikichi):** *Chemical studies on minerals containing rare elements in the Far East (Rep. 51). Gadolinite from Fusamata, Kawamata-machi, Fukushima Prefecture.* Nippon Kagaku Zasshi, **81**, 1054–1055 (1960). (in Japanese)

A greenish black mineral was found in pegmatite at Fusamata. X-ray powder lines are in good agreement with those of gadolinite. The result of chemical analysis is as follows: BeO 3.12, MgO. 0.71, CaO 3.98, MnO 1.34, FeO 11.45, Al_2O_3 0.52, Fe_2O_3 4.36, Ce_2O_3 1.52, $\sum Y_2O_3$ 50.13, ThO_2 0.45, SiO_2 21.30, $(Nb, Ta)_2O_5$ 0.00, H_2O 0.58, total 99.46%. The distribution of rare-earth elements belongs to the thalenite type. The contents of trivalent metals, except Be, are larger than those of typical gadolinite.

3066. **Kato (Toshio):** *Uranothorite from Naégi, Gifu Prefecture.* Miner. Jour., **3**, 90–95 (1960).

Uranothorite from Naégi, Gifu Prefecture occurs as small grains in placers. Colour: Yellowish or reddish brown. Sp. gr.: 4.30. n: about 1.68. The result of chemical analysis of the sample from Nameri, Kitsumizawa follows, CaO 1.16, PbO 0.98, Al_2O_3 1.84, Fe_2O_3 2.54, Ce_2O_3 etc. 1.89, ThO_2 58.17, UO_2 9.05, SnO_2 0.26, TiO_2 0.02, SiO_2 11.89, P_2O_5 0.59, $H_2O(+)$ 7.10, H_2O (−) 4.98, total 100.47%. The main features of the specimen imply that it is a metamictized mineral belonging to the uranothorite-thorogummite series.

Physical Properties of Minerals

3067. **Suzuki (Teruo):** *The measurements of thermo-electric potential of pyrite from the Chichibu mine.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **44**, 171–178 (1960). (in Japanese with English summary).

Thermo-electric potential of pyrite from the Chichibu mine was measured on the electrolytic alloy etched section, of which the results were in good agreement with those of polished section.

Rock-forming Minerals and Petrology

3068. **Banno (Shohei):** *Optic axial dispersion of glaucophanic amphiboles.* Jour. Geol. Soc. Jap., **66**, 357 (1960).

Because of some confusion hitherto made in descriptions on the optic axial dispersion of glaucophanic amphiboles, the present author makes revision, showing the data in graphs.

3069. **Iwasaki (Masao):** *Clinopyroxene intermediate between jadeite and aegirine from Suberidani, Tokushima Prefecture, Japan.* Jour. Geol. Soc. Jap., **66**, 334–340 (1960).

A clinopyroxene intermediate in composition between jadeite and aegirine was found in clinopyroxene-lawsonite schist from Shikoku. It has the chemical composition: SiO_2 52.41, Al_2O_3 9.47, TiO_2 1.56, Fe_2O_3 15.54, FeO 1.43, MnO 0.12, MgO 2.96, CaO 5.06, Na_2O 9.97, K_2O 0.10, $H_2O(-)$ 0.08, $H_2O(+)$ 1.10, P_2O_5 0.06, total 99.86%, with the molecular proportion: aegirine 0.43, jadeite 0.36, diopside 0.17, hedenbergite 0.04. The provisional cell dimensions: $a_0=9.56$Å., $b_0=8.77$Å., $c_0=5.24$Å., $\beta=72°13'$. Space group: $C_{2/c}(C^6_{2h})$. The author attributes its origin to the absorption of silica by the surrounding serpentine, during the metomorphism of the host rock.

3070. **Iwasaki (Masao):** *Colourless glaucophane and associated minerals in quartzose schists from Eastern Shikoku, Japan.* Jour. Geol. Soc. Jap., **66**, 566–574 (1960).

The piedmontite quartz schists which are intercalated in alkali-amphibole schists in the headed district usually contain colourless amphibole. Its chemical composition is as follows: SiO_2 56.89, TiO_2 <0.05, Al_2O_3 7.98, Fe_2O_3 7.43, FeO 0.33, MnO 0.44, MgO 15.53, CaO 0.86, Na_2O 6.51, K_2O<0.10, $H_2O(-)$

0.00, $H_2O(+)$ 3.62, total 99.74%, (analyst, H. Haramura). It is very close to the idealized formula of the magnesium-end of subglaucophane $Na_2Mg_3AlFe^{3+}Si_8O_{22}(OH)_2$. Optical properties: α=1.621, β=1.635, γ=1.637, $2V(-)<20°$, dispersion $\rho>\upsilon$, $c\wedge Z=17°$, X=Y=Z=colourless, yellowish white to the naked eyes. According to the writer's view, the mineral paragensis of the host rock is stable under some reducing environment.

3071. **Kuno (Hisasi):** *Titaniferous pyroxene in hornfels from Shisaka-jima Island, Japan.* Jour. Geol. Soc. Jap., **66**, 616–617 (1960).

A clinopyroxene rich in Ti and Al was separated from the hornfels which have been found as nodules in a thin lense of crystalline limestone in the Shisaka-jima Island. The constituent minerals of the hornfels are titaniferous pyroxene, dark green spinel, magnetite, amphibole, apatite, quartz, chlorite and calcite. The chemical analysis was carried out giving the following results; SiO_2 45.50, Al_2O_3 6.89, Fe_2O_3 3.24, FeO 3.88, MgO 11.81, CaO 25.95, Na_2O 0.12, K_2O 0.04, $H_2O(+)$ 0.58, $H_2O(-)$ 0.11, TiO_2 2.47, P_2O_5 n.d., MnO 0.08, Cr_2O_3 n.d., total 100.67%, (analyst, H. Haramura). Optical properties: α=1.685, β=1.692~1.738, $\gamma-\alpha$=0.020, $(+)2V$=27°~44°, dispersion strong $\rho>\upsilon$, $c\wedge Z=43°$, purplish brown without pleochroism.

3072. **Shimizu (Jiro) and Kuno (Hisasi):** *Anorthoclase phenocrysts in trachyte from Hawaii Island.* Jour. Geol. Soc. Jap., **66**, 547 (1960).

Anorthoclase phenocrysts were separated from the trachyte of a lava dome on the northern flank of Hualalai Volcano in the island of Hawaii and were analysed with the following results: SiO_2 64.85, Al_2O_3 19.36, Fe_2O_3 0.99, FeO n.d., MgO 0.37, CaO 0.56, Na_2O 7.97, K_2O 4.96, $H_2O(+)$ 0.47, $H_2O(-)$ 0.05, TiO_2 tr., total 99.58%, (analyst, H. Haramura). Optical properties: α=1.528, β=1.531~1.532, γ=1.533, $2V(+)$=43°~36°. These values and the results of X-ray analyses agree with those given for members of the high-albite-sanidine series having compositions about $Or_{28}(Ab-An)_{72}$.

Various Topics

3073. **Omori (Keiichi):** *Infrared absorptions of feldspars.* Jour. Jap. Asso. Min. Petro. & Econ. Geol., **44**, 179–186, (1960). (in Japanese)

Infrared absorptions of orthoclase from Naégi, Gifu Prefecture, perthite from Ishikawa, Fukushima Prefecture, moonstone from Korea, albite from Alp Ruscuna, oligoclase andesines from Nagano Prefecture, Naka-Iwo-Jima and Iwo-Jima, anorthites from Tarumaé volcano, Hokkaido and Miyaké-Jima were studied by Perkin Elmer 21 type double beam infrared spectrophotometer. Feldspars have a strong broad band at 8.5~11μ. and some medium sharp bands at 13~15μ., by which high and low types of plagioclases are distinguished.

3074. **Hayase (Ichikazu)**: *Radioactivity of feldspars and biotites in the granitic rocks in the Misasa-Kurayoshi region, Tottori Prefecture.* Bull. Geol. Surv. Jap., 10, 801–807, (1959). (Japanese with English abstract)

The radioactive source of the granitic rocks of the region has been studied by autoradiography and revealed that it is not only distributed in fine grained radioactive minerals but also in main rock-forming minerals, of which the intensity of radioactivity is usually descending in the order of altered plagioclases, fresh sodic plagioclases and potash feldspars in each individual specimens. The age of the radioactive source of the main rock-forming minerals is estimated to be about the same as that of the host granite.

3075. **Sunagawa (Ichiro)**: *Mechanism of crystal growth, etching and twin formation of hematite.* Miner. Jour., 3, 59–89, 14 plates (1960).

The surface structures of hematite crystals from nine localities are observed with an ordinary reflecting and a phase contrast microscope, and the step heights of growth layers as well as the other surface features are measured precisely with multiple-beam interferometric method and the method of fringes of equal chromatic order. On the basis of these observations and measurements, mechanism of crystal growth, natural etching, twin formation and movement of screw dislocations after the cessation of growth and the possibillity of polytypism are discussed in this paper. Physical and chemical conditions under which hematite crystals have grown are also discussed on the basis of characteristics of growth and etch patterns.

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